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PREFACE

Most scientific books represent at best an approximation of an ideal. Especially is this true of the "Encyclopedia of Chemistry"—the first attempt to combine the contributions of hundreds of authorities into a single integrated volume covering the enormous and heterogeneous field of chemistry. The ideal we have sought to achieve is a reference book *par excellence*, in which the vast range of subject matter is correctly weighted, usefully organized, and concisely presented by experts in such a way as to be at the same time scrupulously accurate and highly informative to anyone having a bowing acquaintance with chemistry. There are some who have said that this ideal is impractical—indeed that to compile such an encyclopedia is an impossible task. To what extent we have succeeded will not be determined by either the editors, the contributors, or the publishers, but by those whom the book is intended to serve—the multitude of chemists, physicists, engineers, biologists, research workers, teachers and students who comprise the scientific population of the world.

To capture between the covers of a single volume the sweeping scope and essence of any subject matter as complex and diversified as chemistry is a challenging task of the first magnitude. Now more than ever, analytical, inorganic, organic, physical, biological, engineering, electronic, metallurgical, colloid, and other branches of chemistry, because of sheer size and specialization, seem to go their separate ways in techniques, training methods, and literature, almost as though they were entirely different sciences. The student trying to prepare himself as a chemist in the broadest sense becomes increasingly confused and discouraged in attempting to move in so many directions without an integrating and unifying aid to guide him.

Perhaps, then, it is the primary function of a modern Encyclopedia of Chemistry, especially a single-volume one, to introduce a factor of convergence instead of divergence; focal condensation instead of scattering; unity instead of multiplicity; a centripetal instead of centrifugal process—in a word, *chemistry* instead of a multitude of qualifying terms. It has taken courage and faith to believe that this could be done and humbly to undertake the task of creating a reference work for which there has been, is, and will be such an obvious need on the part of chemists, scientists in general, teachers, librarians, and intelligent and inquiring laymen.

Such an Encyclopedia, if it is to accomplish its mission, cannot be merely a dusty compilation of definitions and data. Despite its necessary brevity of treatment, it must somehow communicate, in an irreducible minimum of words, the living, ever-changing habilitments of one of the greatest areas of organized knowledge. An Encyclopedia prepared by skilled authorities in so many fields can be not only informative but interesting and inspiring in both direct and intangible ways. It can have simultaneously the qualities of timeliness—a true and up-to-date representation of the chemistry of 1956—and timelessness, by which is meant a preparation so sound in terms of fundamentals that there will be no feeling of obsolescence when these articles are read in later years. Expansion, changes, new discoveries, corrections of errors and misconceptions there will inevitably be; but these should constitute merely superstructures on an established and enduring foundation.

These are some of the ideas and ideals upon which the planning, preparation and publication of this Encyclopedia have been founded. The old dream of Francis M. Turner has at last come to fruition.

Coordinated with the unifying and condensing concept is the fact that this is the com-

bined contribution of one of the most capable teams of chemists and allied scientists ever assembled to produce a single volume—great in number (over 500) and distinguished in reputation. The editors might well write a book on their experiences—almost all of them wonderfully pleasant and gratifying—in dealing with this select group. These authors believed from the beginning in the urgent need for a single-volume Encyclopedia of Chemistry; and the busier they were with other responsibilities, seemingly the greater was their interest and willingness to give generously of their knowledge, effort and time with no monetary compensation in order that this undertaking might succeed. Such selfless actions underlie true progress on all fronts of human endeavor.

Many of those who accepted the invitation to contribute felt that we were unreasonable in expecting them to discuss a complicated topic in the small amount of space available; yet there were few cases which required drastic shortening. Most of the articles are near miracles of condensation; and the book is so arranged that, by making use of the cross-references amply provided both within and at the end of the articles, the reader will be able to obtain a quite extensive coverage of any given subject. Inevitably there are omissions and deficiencies; but within the limitations of time set upon preparation so that all articles would remain fresh and most useful, the editors have striven mightily to reduce overlapping of subject matter and other defects to a minimum.

The topics selected for inclusion deal primarily with chemistry proper. However, "chemistry" means many things to many people. Realizing this, the editors have chosen to interpret the term quite broadly, and have included a number of subjects which, though not strictly chemical, either relate closely to the chemistry of materials and processes, or can be treated from a chemical point of view, e.g., Automatic Process Control, Annealing, Abrasion Resistance, Electron Tubes, and Instrumentation. Similarly, chemical engineering has been given appropriate attention; the more important unit operations and the basic theoretical considerations are presented under appropriate headings. Borderline subjects such as Air Pollution, Chemical Economics, Plant Location, and Market Research have also been included to round out the picture.

Besides these there are a number of articles which summarize the scope of other sciences which comprise a sort of "exurbia" of chemistry, such as Potentiometry, Meteorology, Metallurgy, and Bacteriology. These have been described as far as possible from the viewpoint of the chemist, and have been included to help integrate the entire concept of chemistry as it exists in the universe, as opposed to the laboratory, the classroom or the plant. Doubtless many others could justifiably have been added, but here too space limitations were a restraining influence. The same holds true of the brief biographies of outstanding figures in past chemical achievement, and of the information presented on research institutions. It is hoped that these will serve a useful purpose and that no glaring omissions have occurred.

Especially warm appreciation must be expressed to Mrs. Jean Pingry and her successor, Mrs. Margaret Kuo, secretaries at the University of Illinois, for their enthusiastic and faithful management of the very extensive files and correspondence involved in this project. Thanks are also extended to Mrs. Marilyn Nazimowitz for effective record-keeping and proof-checking in the office of the publisher. The editor-in-chief is deeply grateful to his colleagues at the University of Illinois, former students, friends and fellow chemists all over the country for their abiding interest and wise suggestions in helping to create something which might serve as a true panorama of all of chemistry. And without the continuing faith, encouragement and help of his wife through 37 years of literary and scientific effort his part in this project would have been far more difficult and less rewarding.

G. L. Clark
G. G. Hawley

A

ABRASION RESISTANCE

Abrasion resistance denotes the ability of a material to resist wearing of the surface when it is rubbed across the surface of another material. It is not a definitive property. Instead, it is used in a relative sense to rate or rank materials in their order of resistance to frictional wear. The term may be applied to all materials, e.g., metals, mineral products, and organic and fibrous materials, that wear away primarily by loss of matter at the surface through a frictional process. In particular, it is extensively used in rubber technology for comparing the wear characteristics of rubber compounds.

Abrasion resistance cannot be expressed uniquely in terms of the other properties of a material. Hardness is related to some extent to abrasion resistance: diamond is the hardest of materials and has the greatest abrasion resistance; also, the abrasion resistance of steel is increased when it is hardened. On the other hand, hardness is not the only factor governing abrasion resistance, and it is not the most important one in selecting a material for a particular service. For example, steel is much harder than rubber but has a much lower abrasion resistance in many applications.

Similarly, abrasion resistance is related to coefficient of friction only in a broad sense. When the coefficient of friction is very low, wear is very slow; but when it is high, wear is not necessarily rapid. To illustrate, rubber has a higher coefficient of friction than steel against most surfaces, but a lower abrasion resistance under many conditions.

An understanding of abrasion resistance is possible only from a knowledge of the mechanism of abrasion. There are at least two mechanisms involved: (1) the erosion mechanism, or the mechanical or physical removal of the surface layer of a material by chipping, tearing, shearing, breaking, or other physical process; (2) a chemical mechanism in which the surface layer is degraded by corrosion or pyrolysis prior to the removal of material by mechanical or other means. Oxygen is the corrosive agent under most conditions, but other chemicals are responsible for the corrosive action in some instances. Both mechanisms are greatly influenced by the temperature of the surface layer, which depends on the frictional force, rate and amount of slip, and thermal conductivity of the material. The large amount of frictional heat produced during abrasion may raise the temperature of the molecular layer on a surface to such an extent that visible radiation is emitted. At elevated temperatures, the mechanical properties of the material become weaker which makes erosion of the surface easier, and chemical degradation becomes more rapid and extensive. Abra-

sion resistance usually decreases with increase in temperature. However, it is interesting to note that some synthetic rubber tire treads improve in abrasion resistance with an increase in ambient outdoor temperature; the reason for this behavior is obscure.

One or the other of the mechanisms may predominate, depending on the conditions. When abrasion is extremely rapid, the erosion mechanism is generally predominant, particularly if a large temperature rise is not involved. This condition exists in wet grinding and probably in the wear of tires in rock quarries and on some gravel roads. On the other hand, chemical degradation tends to predominate under conditions of very slow abrasion, e.g., wear of lubricated bearings and wear of tires at ordinary speeds on smooth paved roads. This dual mechanism for the abrasion process probably accounts for the observed reversal in abrasion resistance of two materials under different conditions.

The high abrasion resistance of rubber is unique for a material having a low hardness and a high coefficient of friction. The high extensibility and elastic recovery of rubber are probably responsible for this quality. In the case of sand-blast hose, the abrasion resistance is determined mainly by the elastic properties of the rubber compound. However, in the case of tires, the elastic properties are insufficient to explain the abrasion resistance of the treads. Under many service conditions, resistance to chemical degradation apparently is of equal or greater importance. The molecular structure of the rubber molecule, carbon blacks or other reinforcing agents, antioxidants, and vulcanizing agents have effects on abrasion resistance of tread compounds independent of, or in addition to their effects on the mechanical properties.

The average life of passenger car tires in the United States is estimated to be around 30,000 miles. At this rate of wear, there is a loss of 1 gram of tread rubber over an area of about 2×10^7 square centimeters of roadway, equivalent to an average thickness of about 5 Angstrom units. Tread wear tests using radioactive rubber compounds indicate that the tread is worn off sufficiently evenly to reveal a continuous tread pattern on the roadway at rates of wear corresponding to an average thickness of about 2 Angstrom units. This pattern is possible only if the rubber is abraded in molecular layers and the largest discrete particles correspond to the individual particles of black or other fillers.

In a process where successive molecular layers are exposed, oxidation must be an important factor, particularly at the high surface temperatures produced by friction. At high rates of slip on a relatively smooth, dry pavement, the surface temperature becomes high enough to pyrolyze the

rubber, and the pyrolytic products are smeared on the roadway. This abrasion is very rapid even though chemical degradation is the predominant mechanism.

The determination of abrasion resistance has not been satisfactorily solved. Thus far, laboratory tests have not been able to replace tests under service conditions. Nevertheless, laboratory abrasion tests are extensively used; more than 20 different testers have been developed and are in use for measuring the abrasion resistance of organic and fibrous materials. These testers do not rank materials in the same order, presumably because of different conditions of test. The influence of the conditions of test on the abrasion resistance indicate that it depends on many factors. It is interesting to note that all laboratory tests for determining the abrasion resistance of rubber rapidly abrade the rubber mainly as discrete particles, and thus overemphasize the mechanical properties of a material in relation to its resistance to chemical degradation.

In all frictional processes, electrostatic charges are produced as the two materials rub across each other. These charges may have an influence on the abrasion resistance, particularly through their effect on chemical degradation either directly or by the production of ozone. However, the role that electrostatic forces play in the abrasion process is not known.

Plastics, leather, textiles, lacquers and paints are other high-molecular weight organic compounds that are used in applications requiring abrasion resistance. These materials differ from rubber primarily in their extensibility. Their lower extensibility tends to make them less resistant to erosive forces than rubber; their resistance to chemical degradation may be greater or less than that of rubber.

The abrasion resistance of mineral products is governed mainly by their resistance to erosion in most applications. The abrasion resistance of metals is complicated by the oxide film that forms on the surface of many and by the welding that occurs under high pressures and temperatures. Erosion or chemical degradation may predominate depending on the particular abrasive conditions.

ROBERT D. STIEHLER

Cross-References: *Rubber, Carbon Black, Metals*

ABRASIVES

Abrasives are rough, gritty, wear-producing particles, such as the hard dusts that wear down carpets, bearings, etc. Industrial applications of abrasives are varied, as, for example, the sharpening of tools and polishing of materials. Most important is the finishing to precise dimensions of numerous machine parts, such as crankshafts, cylinders, etc. So important is this that the mass production of automobile and other engines would hardly be possible without the modern grinding wheel.

There are both natural and synthetic abrasives. The most common of the former are sand (SiO_2), used for cleaning stone surfaces and to some extent

for small industrial products, and emery (corundum) which is in wide use as a finishing abrasive. More important for precision work is the artificial abrasive, silicon carbide (SiC), discovered in 1891 by Acheson.

Abrasive action may be considered from two viewpoints—grinding and polishing. In grinding, the surface of the work is penetrated by the abrasive, and material is removed, by a process of shear, in the form of plastically deformed chips. Polishing action is quite different. It has been found by Beilby that the top layer of a metal changes after polishing from a crystalline to an amorphous form. In work with sliding solids, Bowden and his co-workers showed that even under light pressures and low rates of rubbing, high temperatures develop at areas of actual contact. These local high temperatures cause softening or melting with consequent smearing or flowing to give the polished Beilby layer. Moreover, harder materials do not necessarily polish softer ones, as would be expected if the action were one of grinding. It is the relative melting points that is important; the solid with the higher melting point polishes the one with the lower melting point, even if it is not as hard. In practice, the division between grinding and polishing is not sharp; e.g., the term "polishing" is applied to operations that range from grinding on a flexible wheel to light buffing.

Chemical reactions not yet elucidated undoubtedly occur. There is some supporting evidence for this view: (1) some abrasives are soluble in metals; (2) the high temperatures and pressures that accompany abrasive action, and the highly reactive state of freshly cut metal, are conducive to reaction; (3) atmospheric oxygen, water vapor and contaminants are present.

Grinding Abrasives. The most important of these are fused aluminum oxide (Al_2O_3) and silicon carbide (SiC). The former is made from bauxite in the arc type electric furnace. The fused mass, after controlled cooling, is crushed and screened to desired size and shape of grain. The product is brown, crystalline, and contains about 95% Al_2O_3 ; the remainder is Fe, Ti and Si oxides. By adding certain impurities to the melt, or by starting with a purified alumina, a more readily fractured grain results. SiC is made in the electric furnace by the reduction of pure silica sand with coke. The fused mass also undergoes crushing, etc., to yield a black or green crystalline grain. Both fused Al_2O_3 and SiC are very hard and tough; SiC has the greater resistance to fracture. Both are highly refractory. An important property is resistance of the abrasive points to wear by attrition. This depends on the work surface; Al_2O_3 is more resistant on hard steel, SiC on cast iron, etc. Fused Al_2O_3 is used for grinding materials of high tensile strength, such as steel; SiC on materials of low tensile strength such as Al and Cu, and on hard, brittle materials like marble, cast iron, etc. The production and use of these two abrasives is far greater than that of any others.

Boron carbide (B_4C), a product of the graphite electric furnace, is the hardest synthetic abrasive; its cost limits its use as an abrasive to lapping

cemented carbides. Bortz diamonds are widely used for polishing gems, dressing diamond wheels, and sharpening carbide tools. Corundum, a naturally occurring alumina, is very hard; its use is in grinding optical glass. Emery, an impure corundum, is used for fine grinding and polishing.

Polishing Abrasives. Many minerals besides emery are used for polishing. Some of the more industrially important are tripoli, an aluminum silicate mixed with Fe and Mn oxides, widely used for buffing brass and Al; red rouge, Fe_2O_3 , used for precious metals, glass and plastics; Vienna lime, a calcined dolomite, used for light buffing of brass, copper and nickel plate; chromium oxide (Cr_2O_3), and fused and unfused Al_2O_3 , for the high finishes on stainless steel; pumice, an aluminum silicate, for plastics and glass bevelling; garnet, a mixture of Fe, Ca and Al silicates, and quartz, used as coated abrasives.

Abrasive Products. (1) Nearly all grinding wheels use either fused Al_2O_3 or SiC. The grains are carefully dispersed in suitable binders, called bonds. These are either vitrified (mixed clays), sodium silicate, shellac, resinoid (usually phenolic or phthalate), or rubber. By close control, wheels of any desired strength and kind of bond, and grain spacing, may be made. By varying also the kind and size of the abrasive grains, the manufacturer offers a very large selection of wheels from which almost any grinding requirement may be met. (2) Coated abrasives are made by depositing abrasive grains on paper or cloth, with glue or a water-proof resin as adhesive. The older gravity feed has been replaced by an electrostatic process of deposition, resulting in more uniform dispersion and more effective orientation of grain. Coated abrasives in the form of endless belts have become of increasing importance for flexible grinding and polishing. (3) Polishing wheels are made of discs of either cotton sheeting, canvas, felt, or leather, sewed together. Hide glue or sodium silicate solution is applied to the wheel face, and then the abrasive grain, usually fused Al_2O_3 , or emery for some fine finishes, is embedded in the adhesive. When the wheel loses its cutting action the face is re-coated. (4) The abrasives commonly used in buffing compositions and pastes are emery, tripoli, lime, rouge, silica, Cr_2O_3 , fused and unfused Al_2O_3 . The binders are usually mixtures of stearic acid, tallow, petrolatum, waxes, or glue. There are numerous other products, e.g., shot in sand-blasting, various grains and products in tumbling barrels for burnishing, sharpening stones, aqueous polishing suspensions, etc.

BENJAMIN FREEMAN

Cross-references: *Aluminum Carbides, Hardness, Abrasion Resistance*

ABSORBENTS

Absorbents are substances having the capacity to take up other substances by the process of absorption, i. e., the penetration of one substance (the absorbate) into the inner structure of another (the absorbent), with a resulting loss of identity of the original substance. Either the absorbate

merely dissolves in the absorbent, as in the solution of hydrogen chloride gas in water to form hydrochloric acid, or it reacts chemically with the absorbent, as in the absorption of carbon dioxide by sodium hydroxide solution, yielding sodium carbonate. By the reverse process of desorption, or stripping, the absorbed materials may sometimes be recovered in their original form. For instance, passing air through a solution of hydrochloric acid liberates hydrogen chloride, and the treatment of sodium carbonate with an acid regenerates carbon dioxide.

Absorbents are widely used in both laboratory and large-scale operations for the concentration and recovery of desirable materials, or for the elimination of interfering, obnoxious, or otherwise objectionable substances. Very often they are selective, so that only a specific constituent is removed from the gas or liquid stream for subsequent regeneration or discard.

Types of Absorbents. The effectiveness of the *nonreactive* absorbents depends on the relative resistances of the fluid films adjoining the interface between the absorbate and the absorbing medium, the relative motion of the two fluids, and the solubility of the solute in the absorbent. It is only with proper engineering of the absorption apparatus to bring the separate phases into intimate contact that maximum efficiency can be achieved. The usual effect of increasing temperature is to diminish the solubility of a gaseous component. Solubility is further reduced by the increasing concentration of solute in the absorbent. Relatively large quantities of the nonreactive absorbents and well-designed equipment are required. Water is generally used in this type of absorption because it is the most available and the cheapest solvent. If the material to be absorbed is not soluble in water, other solvents must, of course, be used. With nonreactive absorbents, the absorbate is rather easily stripped or desorbed by such physical processes as heating, flushing with an inert gas, or fractional distillation.

Absorption by chemical reaction is often the most economical method, since virtually complete absorption is possible with minimum amounts of the *reactive* type of absorbent. Although intimate contact between phases is necessary, the limiting factor is only the rate of reaction, which is controlling if the reaction takes place slowly. The rate of absorption is then equal to the rate of reaction. If the reaction is rapid, as in most instances, the chemical resistance is small, and the diffusional resistances are controlling, just as though no chemical reaction were involved. A second chemical reaction may be required to liberate the absorbed material, but this is not usually objectionable. In some processes, it is advantageous to use as an absorbent a liquid compound or a solution which reacts with the gas to be absorbed, forming a loose chemical compound which may readily be decomposed.

For laboratory applications, such as the analysis and purification of gases, the recovery of vapors, or the elimination of obnoxious fumes, absorption is easily accomplished by passing the stream through bubble towers, absorption tubes,

contact pipettes or other apparatus containing the absorbent material. Some of these have been developed and improved for such specific purposes as direct weighing of the absorbed constituent, regeneration of a gas, or the simultaneous absorption of two or more gases. Some of the more common absorbents for laboratory use are given below.

Absorbent	Absorbate
Water	Soluble gases and vapors (HCl, NH ₃ , alcohols, etc.)
Ascarite (NaOH asbestos) or Soda-lime (NaOH-CaOH)	CO ₂ , H ₂ S, and other acidic gases
Acid cuprous chloride or Cuprous sulfate-beta naphthol in H ₂ SO ₄	Carbon monoxide
Alkaline pyrogallol, Chromous chloride, or Sodium hydrosulfite	Oxygen
Fuming H ₂ SO ₄ + SO ₃ or Bromine water	Unsaturated hydrocarbons

Equipment for Absorption. Because of the wide variety of purposes and specifications of industrial absorption equipment, a very large number of different types are in use. The objective of each design, however, is the promotion of intimate contact of gas and liquid over a large interphase surface, to produce a high rate of absorption with a minimum quantity of absorbent. The various types may be divided into three groups: (a) plate or bubble-cap towers, (b) packed towers, and (c) miscellaneous types, including spray towers. Equipment of the same basic design is effective also for the desorption of the non-reactive absorbates, since intimate surface contact is the prime factor. Solid absorbents, extremely useful in small-scale operations because of the high flow rates permissible, are not commonly utilized in industrial absorption processes because of the prohibitive cost of manufacture and handling.

C. W. CHAGNON

ACCELERATORS

Accelerators are substances (usually nitrogen containing organic compounds) which increase the rate of vulcanization of rubber. A major difficulty in the early history of the rubber industry was the slowness with which rubber and sulfur reacted. This difficulty was complicated by fluctuations in the vulcanization rate in different batches of rubber, due to variation in the content of nitrogenous materials. In 1900 it took about four hours to vulcanize a tire, and then there was a possibility that it would be overcured or undercured. Early research in the rubber industry was directed, therefore, toward finding materials which would accelerate the rate of vulcanization. These materials are called "accelerators" and are further defined in terms of their ability to perform this function. Thus, those materials which reduce the vulcanization time from several hours

to a few minutes are called ultra-accelerators and those which are somewhat slower are referred to as semiaultra-accelerators. It was later found that accelerators possessed other desirable features. Thus, the sulfur requirements could be reduced from as much as 10 per cent to 2 or 3 per cent, based on the rubber content of the mix. In cases where sulfur was available in the accelerator, such as the thiuram disulfides, the sulfur requirements were reduced to 1 per cent or less. A direct correlation exists between the amount of combined sulfur in vulcanized rubber and the rate of deterioration of rubber in air. Therefore, the use of accelerators which require less sulfur yields products with greatly improved aging properties. In general, accelerated vulcanization enhances the physical properties of the vulcanized rubber, due in part to the reduction in thermal degradation of the rubber which takes place independently of vulcanization.

Certain accelerators have the property of broadening the vulcanization time for optimum cure. This is called the plateau effect. Normally the physical properties such as modulus and tensile strength increase, go through a maximum, and then decrease. Because thick articles do not cure uniformly due to the poor heat conductance of rubber, the plateau effect becomes very important. An additional advantage of the short vulcanization time is the possibility of incorporating organic dyes, which normally decompose under prolonged heating at elevated temperatures.

Classification. The first accelerators were the basic carbonates and oxides of lead, supplemented by other basic metal oxides or hydroxides such as magnesia or lime. The first organic accelerator was aniline (Denslager in 1906). Other amines were also used, and were followed shortly by their derivatives such as thiocarbamide, hexamethyl enetetramine and various reaction products of amines with aldehydes as well as the diarylguanidines. Amine derivatives, such as the dithiocarbamates and thiuram sulfides of secondary alkyl amines, were developed to form a class frequently called "ultra-accelerators" because of their high accelerating activity. In fact, their activity was so great that in most cases it was found to be impracticable to use them because of their tendency to cause premature vulcanization. The most important class of organic accelerators developed was the thiazole-thiols, particularly 2-mercaptobenzothiazole and its derivatives. These now, dominate the field and constitute more than 70% of all accelerators manufactured. Another class, characterized by having no nitrogen in their composition, includes the xanthates, the dithiocarboxylic acids and their derivatives. These, because of relatively poor stability and tendency to prevulcanize at low temperatures, have been of little practical value. Some of the more useful members of the various classes are considered below.

Aldehyde-amines. The aldehyde-amines are made usually from aniline reacted with such aldehydes as formaldehyde, acetaldehyde, butyraldehyde, heptaldehyde etc, or combinations of two or

more such aldehydes. They are liquid or resinous products of somewhat uncertain composition and their use is largely as activators with thiazole-type accelerators, in hard rubber and other specialties.

Guanidines. The guanidines, diphenyl or di-*o*-tolyl, are white crystalline materials obtained by reacting aniline or *o*-toluidine with cyanogen chloride. They are used extensively as activators with thiazole-type accelerators, particularly in GR-S tire stocks.

Thiuram sulfides. Tetramethylthiuram disulfide is the most important member in this class. It is a white crystalline solid obtained by oxidizing dimethyldithiocarbamic acid with hydrogen peroxide, nitrous acid or other oxidizing agents. It is used largely in GR-I (butyl rubber) inner tubes as well as an activator with thiazole accelerators. This accelerator also is useful as a curing agent without additional sulfur to provide rubbers having no free sulfur and excellent aging characteristics.

Tetramethylthiuram monosulfide is a yellow crystalline product obtained by treating the corresponding disulfide with sodium cyanide. It has the same general uses as the disulfide but has less tendency to vulcanize prematurely.

Dithiocarbamates. A number of metal salts of various dithiocarbamic acids are used as accelerators. Most important are zinc dimethyl- and zinc diethyldithiocarbamates. The former is used largely as an activator while the latter is used extensively in latex foamed rubber. The salts are prepared by adding carbon disulfide to an aqueous solution of the amine and sodium hydroxide. On addition of zinc chloride, zinc dithiocarbamate precipitates.

2-Mercaptobenzothiazole. 2-Mercaptobenzothiazole and its derivatives have been the outstanding accelerators in the tire manufacturing field, not only because of the excellent results obtained by their use in rubber but also because of their ease of manufacture and relatively low cost. The parent compound, 2-mercaptobenzothiazole, is readily prepared by heating carbon disulfide, aniline and sulfur in an autoclave at about 250°C. Its use as an accelerator is second only to that of its own derivatives. One of the earlier and more generally used accelerators which overcame the precuring or "scorching" difficulty was 2,2'-diethyldithiobenzothiazole, obtained by the oxidation of mercaptobenzothiazole. In recent years the introduction of the highly reinforcing and somewhat alkaline furnace blacks has caused the scorching problem to become more acute. To overcome this, another type of mercaptobenzothiazole derivative has been developed and is growing in popularity. This is the sulfenamide in which the thiol hydrogen of the mercaptobenzothiazole is replaced by an amine attached through the nitrogen to the sulfur. Two derivatives which are in commercial use today are *N*-cyclohexyl-2-benzothiazole sulfenamide and *N*-oxydiethylene-2-benzothiazole sulfenamide. The sulfenamides are prepared by the oxidative action of sodium hypochlorite on a mixture of mercaptobenzothiazole

and the amine or by the action of chlorine on a solution of sodium hydroxide, mercaptobenzothiazole and the amine. The greatest drawback to this type of accelerator is the lack of stability during storage.

Specifications. For an accelerator to be accepted commercially, it must satisfy many requirements. It must blend with the rubber uniformly. This factor is controlled by the solubility of the accelerator in rubber, as well as its melting point and particle size. The accelerator, as such, must not affect the appearance of the product; that is, it should not darken light stocks, nor should it bloom to the surface on standing. Solids are preferred to liquids. Accelerators should not have an objectionable odor, should be nontoxic and relatively nonirritating. Finally, it must be stable enough to keep in a storeroom for a reasonably long period of time.

Mechanism of Action. Some progress has been made toward elucidating the mechanism by which accelerators increase the rate of vulcanization. It is fairly well established that most forms of sulfur vulcanization take place by a free radical mechanism. Thus, it is known that the thiuram disulfides and mercaptobenzothiazole generate free radicals under vulcanization conditions. Their function probably lies in the breaking of the stable eight-membered sulfur ring. It is also known that aniline and the thiuram monosulfides form polysulfides which revert to the monosulfide and at the same time liberate active sulfur. Presumably the active sulfur combines readily with the rubber. It is believed that the sulfenamide accelerators decompose to mercaptobenzothiazole, which acts in its usual manner as an accelerator. The delaying action, therefore, comes in the time required to establish conditions under which the decomposition will take place.

R. P. DINSMORE

Cross-references: *Free Radicals, Sulfur, Rubber, Vulcanization*

ACETATES

Acetates are compounds derived from acetic acid (CH_3COOH) by replacing the acid hydrogen with a metal or a radical, so that the resulting compound contains the acetate radical (CH_3COO). The acetates of commercial importance are cellulose acetate, from which "acetate" rayon and many molded plastic articles are made; vinyl acetate, an ingredient of many common plastic articles; and ethyl acetate, used as a solvent in lacquer manufacture.

Cellulose acetate first became commercially important during World War I, when it was used as a substitute for nitrocellulose in airplane dope. Nitrocellulose, or Celluloid, burns with almost explosive violence, and cellulose acetate, which burns with difficulty, was developed to overcome this hazard. At the end of the war, demand for cellulose acetate collapsed, and very little use for this material was found until the introduction of acetate rayon in 1924. Growth of this industry was

slow at first, but by the early 1930's acetate rayon was well established and growing rapidly. 83,000,000 pounds were produced in 1938, and over 250,000,000 pounds in 1955.

Shortly after the introduction of acetate rayon, the injection molding process was introduced in the plastic industry and cellulose acetate was one of the first materials to be used in this new field. This use of cellulose acetate grew rapidly, and it is estimated that more than 100,000,000 lbs. of cellulose acetate and derivatives were used in the plastic industry in 1955.

Cellulose acetate is made by esterifying the hydroxyl groups in cellulose with acetic anhydride. Cellulose from wood pulp or cotton may be used. Cotton is more uniform, and gives stronger products, but wood pulp, which is cheaper, is suitable for many uses. A pretreatment of the cellulose is generally used to swell and disrupt the fibers and assist penetration of the acetylating mixture. Pretreating for several hours with acetic acid or acetic acid to which a small amount of sulfuric acid is added is customary.

Direct esterification with acetic acid requires very drastic conditions, which result in excessive degradation of the cellulose molecule. For this reason, acetic anhydride is used, generally with sulfuric acid as a catalyst. The acetylation reagent consists of a mixture of acetic acid, acetic anhydride and sulfuric acid catalyst. A slight excess of anhydride is used. The acetic acid acts as a solvent for the product. The reaction is exothermic, and some degradation of the cellulose always results. The degree of degradation is controlled by temperature, catalyst etc., and can be estimated by the viscosity of the solution or "dope". (See Esters.)

The acetylation of cellulose proceeds from the outside of the fiber inward, and acetylation to the theoretical tri-ester stage is required before the fiber structure is sufficiently destroyed to form a uniform and homogeneous product. Since such high acetyl ratios are not desired in most products, it is common practice to first acetylate to the tri-ester stage, then hydrolyze the product back to the desired acetyl content, which is generally about 2.0 to 2.6 mols of acetic acid per cellulose unit.

Hydrolysis of the acetylated cellulose is accomplished by adding water to the acetylation mixture. It can be speeded up by addition of more water, or stopped by neutralizing the sulfuric acid catalyst with sodium acetate.

When hydrolysis has proceeded to the desired stage sodium acetate is added, and the product is precipitated by diluting carefully with water. As the precipitation point is reached acetic acid is substituted for water. The precipitate is carefully washed free of acid and salts, as traces of these can cause discoloration or further degradation of the product.

Cellulose acetate is white, odorless and non-toxic. It is generally manufactured in a range of from 53% to 62.5% combined acetic acid for fiber use, and a somewhat wider range for use in plastics. For the production of fibers, the cellulose acetate is dissolved in acetone and formed into fila-

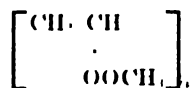
ments by pumping the solution through tiny holes in a "spinneret". The filaments formed in this way are heated to drive off the solvent. It is formed into films by coating a revolving drum with solution, and stripping off the film after evaporation of the solvent. Thicker sheets are formed by extruding viscous concentrated solutions.

Cellulose acetate for plastic use is made into molding compounds which are mixtures of cellulose acetate, plasticizers and usually dyes or pigments. Plasticizers are relatively inert, high-boiling liquids, and may constitute 10% to 70% of the molding compound. The ingredients are blended in mechanical mixers, at elevated temperatures, and the resulting compound is formed into granules or pellets of various size suitable for extrusion or molding.

Cellulose acetate fibers have good stability, are easily dyed, have good strength and wearing qualities. Cellulose acetate plastics are characterized by high mechanical strength and toughness, and are widely used in toys, cutlery and tool handles, radio and appliance housings and as a base for pressure sensitive tapes.

Vinyl acetate ($\text{CH}_3\text{CO} \cdot \text{CH}:\text{CH}_2$) is a colorless liquid with a sharp penetrating odor. It is manufactured from acetic acid and acetylene. In the vapor phase process, acetylene and acetic acid are passed over charcoal impregnated with cadmium or zinc salts, at a temperature of 200°C. A large excess of acetylene is used which, after removal of the vinyl acetate, is recirculated.

Vinyl acetate does not polymerize in the absence of light or catalysts, but when a small amount of a peroxide is present, the polymerization may reach explosive violence. The structure of polyvinyl acetate is represented by the following formula.



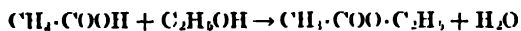
As the molecular weight increases, the polymers change from viscous liquids to tough, horny solids. Vinyl acetate may be copolymerized with other vinyl compounds, or with other monomers, to form a great variety of modifications. Polyvinyl acetate is readily hydrolyzed to polyvinyl alcohol, which in turn may be condensed with aldehydes to form polyvinyl acetals. Polyvinyl acetate is the commercial source of these derivatives, which are used for a variety of specialized applications.

In addition to bulk polymerization, vinyl acetate may also be polymerized in solution in a solvent such as benzene, or in the form of an aqueous emulsion. In aqueous systems, very high molecular weight polymers can be obtained, and the particle size of the dispersed polymer can be varied over a wide range.

These aqueous dispersions are useful as adhesives and protective coatings. They are not affected by wood gums or resins, oils, mild acids or alkalis, and make excellent sealers for wood, paper wallboard and masonry. Vinyl acetate dispersions are also widely used as interior wall paints.

The solid resins are used in chewing gum, phonograph records and plastic novelties. Because polyvinyl acetate has rather poor dimensional stability it is commonly used in applications where fillers or other resins may be added. Solutions of the resin are used in lacquers, paper coatings and adhesives.

Ethyl acetate is widely used as a low-boiling solvent in the manufacture of lacquers. It is a good solvent for many types of resins, has good tolerance for dilution with toluene, xylene and alcohols. Ethyl acetate is one of the best solvents for cellulose nitrate, but will not dissolve cellulose acetate unless some alcohol is present. Mixtures containing up to 15% ethyl alcohol are frequently used as solvents for both cellulose acetate and nitrate. Ethyl acetate is produced commercially by esterification of ethyl alcohol and acetic acid, using sulfuric acid as a catalyst:



In a continuous process, acetic acid, 66°Bé, sulfuric acid and an excess of 95% ethyl alcohol are mixed in reaction tanks until esterification equilibrium is reached, then pumped to a receiving tank. The mixture of crude ethyl acetate in the receiving tank is fed through a preheater to the upper section of a bubble cap plate column. The top of this column is maintained at about 80°C by introduction of steam at the bottom of the column. The vapor from this column, which consists of alcohol, ester and about 10% water, is fed to a second separating column which is operated with a top temperature of 70°C. The vapor from the top of this column is the ternary azeotrope, consisting of 83% ester, 9% alcohol and 8% water. Liquid from the base of the column is returned to the first column. The azeotropic mixture is fed to a decanter, where it is mixed with water to form two layers. The upper layer consists of 93% ethyl acetate, 2% ethyl alcohol and 5% water. The lower layer contains a small amount of ethyl alcohol and ester, and is returned to the separating column for recovery. The upper layer is purified in a third fractionating column, in which the overhead is the ternary mixture, and the bottoms consist of 95–100% ethyl acetate.

ROBERT S. ARIES

Cross-references: *Cellulose; Plastics; Fibers, Synthetic*

ACETYLENE

Acetylene is a colorless gas of molecular weight 26.04. It is the first of the acetylenic hydrocarbons and has the formula $\text{CH}\equiv\text{CH}$. It has a melting point of -82°C at 1,227 mm and a boiling point of -75°C at the same pressure. It is a highly endothermic compound, capable of being formed from most other hydrocarbons at high temperatures (in excess of about 1,500°K). While the free energy of all other hydrocarbons increases with increasing temperature, the free energy of acetylene decreases, following approximately the equation: ΔF (g cal/gm mole) = $54,900 - 13.6 T^\circ\text{K}$

Because of its high heat of formation, acetylene has been a popular source of fuel for welding operations during the past half century. The temperature of the oxyacetylene flame is 6,000°F. In the past quarter century, acetylene has become increasingly useful as a raw material for other organic chemicals. Acetylene production for recent years is listed below.

Year	Thousand Cubic Feet
1935	1,143,199 ^a
1941	2,030,530
1943	5,603,897
1944	6,105,918
1946	3,649,873
1948	5,987,643
1950	5,331,000
1952	5,978,000

It is estimated that by 1970, the total acetylene demands in the United States will be about 2.5 billion pounds, about 80% of which will be for organic chemicals and 20% for fuels.

Manufacture. The commercial method for the manufacture of acetylene until about fifteen years ago was by the reaction of calcium carbide and water: $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$. The calcium carbide is produced in an electric arc furnace from lime and coke according to the reaction: $\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}$. Currently, there are three other important processes, two of which are in commercial use. The Schoch process, developed at the University of Texas by Dr. E. P. Schoch and associates consists essentially of an electrical discharge in an atmosphere of gaseous or vaporized hydrocarbons. The raw materials may be anything from methane to a light kerosene cut. This process is not in commercial use at present.

The Sachsse process consists of a partial oxidation of preheated hydrocarbon (usually natural gas) by preheated oxygen. The oxidation of part of the hydrocarbon liberates the heat required to obtain the required high temperatures. The by-products, carbon monoxide and hydrogen, may be used for various syntheses. The oxidation may also be accomplished by preheated air, in which case the manufacture may be more economical, but the purification more costly. At present, there are at least three major acetylene installations manufacturing acetylene by partial oxidation.

The Wulff process uses a regenerative furnace to rapidly heat a hydrocarbon to 1,000–1,300°C, depending on the charge. The feed may be anything from methane to gasoline. The contact time required is about 0.1 second. The required heat is obtained by burning part of the charge in one furnace while the other one of a pair is cracking another part of the feed. There is one commercial installation for the manufacture of acetylene by the Wulff process.

The reported cost of purified (98%) acetylene is in the range of 5.8 to 10.5¢ per pound depending on the raw material, manufacturing process and purification process.

Of the total acetylene currently consumed as a chemical intermediate, vinyl chloride takes 30%, neoprene takes 28%, trichloroethylene takes 20%,

acrylonitrile takes 10%, vinyl acetate takes 8%, and 4% is taken by miscellaneous processes. The percent of the above five products made from acetylene are 55%, 100%, 95%, 50%, and 100%, respectively. Vinyl chloride may also be made by direct thermal chlorination of ethane or ethylene or the chlorination and subsequent dehydrochlorination of ethylene. Acrylonitrile is also made by the addition of hydrogen cyanide to ethylene oxide, followed by dehydration. A low sales volume, but nevertheless important product, polyvinyl pyrrolidone, is made from acetylene, formaldehyde and ammonia. This chemical has served since World War II as a synthetic blood plasma.

G. E. MONTES

Acetylene Compounds

Characteristics of the Triple Bond. Whereas ethylene has one normal σ bond and one π bond, acetylene has two π -electron bonds along with the ordinary σ bond. The electrons in the C—H bonds and in the normal C—C bond move in overlapping hybridized sp orbitals. This stabilizes the molecule, and shortens the C—C distance to 1.2 Å. One result of this overlapping and shortening is that the C \equiv C bond is stronger than the C=C bond. For example, the C \equiv C bond exists under temperature conditions which rupture the C=C and C—C bonds. In fact, the pyrolysis of saturated and olefinic hydrocarbons is one commercial route to acetylene.

Triple bonds are generally more reactive toward nucleophilic reagents (e.g., water, alcohols, amines, etc.) than are double bonds; that is, the electrons of the triple bond are more electrophilic in character than are the electrons of ethylenic bonds. The reverse is true for electrophilic reagents such as halogens, ozone, peracids, etc. This is explained by the fact that the π electrons of the acetylenic bond are concentrated more nearly in the center of the carbon-carbon bond. This arrangement of the triple bond π electrons then accounts for the much greater acidity of the ethynyl hydrogens. Because of the planar, symmetrical configuration of the acetylenic bond, the π electrons are not polarized as readily as are corresponding ethylenic electrons.

The acetylenic bond resembles the benzene ring in electron withdrawing power, i.e., it is an "electron sink". This electronic effect is illustrated by the fact that α -acetylenic carboxylic acids, such as propiolic acid (acetylene monocarboxylic acid), are very powerful organic acids ($pK_a = 1.4 \times 10^{-2}$). The ionization of propiolic acid is about the same as that of chloroacetic acid, and is 250 times greater than the ionization of the corresponding olefinic acid (acrylic acid). Another example of this effect is the reactivity of the hydroxyl group in a tertiary acetylenic carbinol. Because of the inductive effect of the triple bond, the hydroxyl group resembles that of a saturated secondary alcohol in reactivity.

Additions to the Triple Bond. General remarks. Many substances add across the triple bond of acetylenic compounds. Among these are hydro-

gen, halogens, HX, water, HCN, acrylates, and carbonate esters. The halogens and halogen acids will add in the absence of catalysts. Best reactions are obtained if a catalyst is used. The function of catalysts is to "activate" or polarize the acetylene. Among the important products obtained by such reactions are trichloroethylene, vinyl chloride, acetaldehyde, acetone, acrylonitrile, etc.

Hydration. Hydration of the acetylenic bond is usually carried out with a mercury salt acid catalyst (such as $HgSO_4-H_2SO_4$). The exact nature of the intermediate acetylenic-catalyst complex is unknown. There is considerable evidence that some such coordination compound is the active species. Acetylene itself forms acetaldehyde under the conditions. When a zinc oxide-vanadium pentoxide catalyst is used, acetone is the chief product. (See **Hydration**).

Hydrogenation. Stepwise hydrogenation can be accomplished by proper choice of catalysts. "Poisoned" palladium is used to convert acetylenes to olefins. Mild conditions of pressure and temperature are required. Complete hydrogenations occur when nickel, iron, platinum, or palladium catalysts are used under more drastic conditions. (See **Hydrogenation**).

Diels-Alder Reactions. Diels-Alder type additions are difficult unless the acetylenic bond is activated (polarized) by an adjacent group. In compounds such as propyl ethynyl ketone and ethyl propiolate the triple bond is a good dienophile. For example, the above ketone reacts with butadiene at 120°C to form 2,5 dihydrobutylophenone in nearly quantitative yield. In compounds which contain conjugated olefinic and acetylenic bonds, the acetylenic bond can take part in Diels-Alder reactions as part of a diene system. In such cases only one pair of electrons of the triple bond enters into the reaction. (See **Diels-Alder Reactions**).

Vinylation. This is a special case of addition across a triple bond. The two most important vinylation reactions involve (1) organic acids and (2) alcohols, to form vinyl esters and ethers, respectively. Vinyl esters are prepared commercially on a very large scale for use as monomers. The most important of these is vinyl acetate. Vinyl ethers are being developed as monomers.

Vinylation of acids is carried out by three different techniques. (1) Reactions of acids with acetylene(s) in the vapor phase at 170–250°C over supported catalysts containing zinc and/or cadmium salts result in very high ester yields. (2) Direct vinylation can occur in liquid phase at atmospheric pressure and at moderate temperature (<100°C) in the presence of mercury salt-acid catalysts. (3) Liquid phase vinylation can be carried out at elevated temperatures and under acetylene pressure using soluble zinc and/or cadmium salts as catalysts. Xylene, cyclohexane, etc., are useful solvents. This is one of the so-called Reppe reactions. The compressed acetylene is diluted with an inert gas such as nitrogen to decrease the danger of spontaneous decompositions. Reppe demonstrated that by observing certain precautions, acetylene can be used fairly safely under rather severe conditions. The chief

disadvantage of this process is that the rate of reaction is slow. This means that a given size reactor vessel produces a relatively small amount of product per unit time.

Vinylation of alcohols is also due to Reppe. Primary alcohols add across acetylene at atmospheric pressure in the presence of basic catalysts such as potassium hydroxide to form vinyl ethers. Some secondary and all tertiary alcohols require elevated temperature and acetylene pressure. The base is presumed to function by polarizing or partially ionizing both reagents. Vinyl ethyl ether can be formed by such a reaction scheme, and is used as a general inhalation anesthetic.

Acetylenic bonds can undergo a form of self-vinylation reaction. When acetylene is treated with a cuprous ammonium chloride catalyst, one molecule adds across another so that vinyl acetylene is formed. The chief by-product is divinyl acetylene. Treatment of vinyl acetylene with HCl results in chloroprene. This reaction was discovered by Nieuwland, and is of great importance due to the fact that polychloroprene is the neoprene rubber of commerce.

Another self vinylation reaction was discovered by Reppe. When compressed acetylene is heated in the presence of a nickel catalyst, (e.g., nickel acetylacetonate) in tetrahydrofuran solvent, four molecules of acetylene react to form cyclooctatetraene in 75-85% yield. The chief difficulty with this reaction is that it is apparently very sensitive to "poisons". A similar reaction, which may also be considered as a special case of the Diels-Alder reaction, involves acetylene and butadiene to produce cyclooctatriene.

Substitutions. Acetylenic bonds containing at least one ethynyl hydrogen represent a special case in which the rather positive hydrogen can be replaced by other elements. Alkali and alkaline earth metals react to liberate hydrogen and form the metallo derivatives. The corresponding metal amides react similarly, liberating ammonia. In the first reaction, use of free metal causes reduction of some of the acetylenic compound. Consequently the second method has been more widely used. Thus the classical method of preparation of sodium acetylide is by passing acetylene into a liquid ammonia solution of sodium amide (formed *in situ*). Calcium, lithium, potassium, and barium derivatives have also been made in this manner.

Salts and oxides of I-B metals react to form acetylides. Cuprous, cupric, mercuric, silver, and gold acetylides form readily in neutral or basic media. All these compounds are potentially explosive, but can be used safely under certain conditions. Cuprous acetylide is perhaps the most important of these, and was used by Reppe and other workers as a catalyst for ethynylation reactions.

Grignard reagents are formed readily, and resemble alkali metal acetylides in many reactions.

Ethynylations. Compounds containing at least one ethynyl hydrogen can add across polarized bonds to produce new acetylenic compounds. One of Reppe's contributions to acetylene chemistry is the technique for reacting acetylene with

formaldehyde to produce propargyl alcohol and butynediol. The points of greatest technical significance are that pressure acetylene reactions can be conducted if the acetylene is diluted with an inert gas, and that wet supported cuprous acetylide is safe enough for use as a catalyst.

Ethynylation of aldehydes and base-sensitive (i.e., unsaturated) ketones is best carried out using a metal acetylide in ammonia. Calcium or lithium acetylides are more expensive than sodium acetylide, but since they are less basic, they give higher yields of desired products and less aldol condensation by-products. These reactions are not catalytic.

A third important ethynylation technique uses stoichiometric or excess powdered potassium hydroxide as condensing agent. The function of the base is subject to dispute. It either reacts with the acetylenic compound to produce the potassium acetylide as the reactive species, or more likely it merely polarizes the acetylenic bond to a reactive state. An ether such as ethyl ether, acetal, or a polyether can be used as liquid medium.

T. F. RUTLEDGE

Cross-references: *Carbon Monoxide, Catalysis, Ore Process*

ACHESON, EDWARD GOODRICH (1856-1931)

Acheson at an early age took an unusual interest in the operation of the furnace, did a little amateur prospecting in the hills of Armstrong County, and carried on what might be termed extracurricular activities in mathematics, with special emphasis on geometry, trigonometry, and surveying.

In 1872 when the country was on the threshold of a panic, his father had already suffered financial reverses, and Acheson, who had not yet celebrated his seventeenth birthday, was forced to turn his back upon school and seek a job.

Western Pennsylvania was rapidly becoming industrialized, being crossed by railroads and dotted with coal mines, oil wells, blast furnaces, as well as numerous factories and retail establishments of one sort or another. Acheson's employment, for the next seven years took him far afield and found him in such varied occupations as time-keeper, salesman, ticket clerk, oil-tank gauger, and surveyor.

This provides the background, minus countless struggles and heartaches, for the young man who was destined to become an important aide to Thomas A. Edison; the inventor of an anti-induction telephone cable which he sold to George Westinghouse; the designer of an electric resistance furnace of great commercial significance; the discoverer of silicon carbide ("Carborundum"), the abrasive so important in mass-production machining operations; the first to establish a practical means for the large-scale conversion of amorphous carbon to the graphite allotrope, which process made possible the manufacture of electrodes so indispensable in electrochemistry and electrometallurgy; and a pioneer in the field of colloid chemistry, develop-

ing methods for reducing graphite and other solids to colloidal dimensions and subsequently adapting these colloids to a wide and diversified range of industrial applications.

In addition to the products cited above, Acheson brought into being many other materials and devices for which the United States Government granted him some seventy patents.

Not satisfied simply to create, Acheson, eager to put his creations at the disposal of mankind, founded companies for the manufacture of abrasives, graphite powders, graphite electrodes, inks, and colloidal suspensions of graphite. Numbered among these are The Carborundum Company, Niagara Falls, N. Y.; the Acheson Graphite Company, Niagara Falls (now a part of National Carbon Company, a division of Union Carbide and Carbon Corporation); Acheson Colloids Company, Port Huron, Michigan; and Acheson Colloids Limited, London, England.

During his lifetime, Acheson had numerous honors and awards bestowed upon him. In addition to having received the John Scott Medal on two occasions, he was also awarded the Count Rumford Medal, the Perkin Medal, and his own Acheson Medal. In 1928 he founded the Edward Goodrich Acheson Fund, which, under the trusteeship of The Electrochemical Society, provided a cash prize and the Edward Goodrich Acheson Medal "to the person who, in the judgment of the directors of the Society, shall have made such contribution to the advancement of any of the objects, purposes or activities, fostered or promoted by the Society, to merit such an award." The Society unanimously voted him the first recipient of his own medal for his contributions to electrothermics.

The degree of Doctor of Science was conferred upon Acheson by the University of Pittsburgh in 1909, and five years later he was appointed an officer of the Royal Order of the Polar Star by the King of Sweden.

RAYMOND SZYMANOWITZ

Cross-references: *Allotropes, Graphite, Colloid Chemistry*

ACID NUMBER

Acid number or acid value is a chemical term used to express the degree of acidity of a substance. It is defined as the number of milligrams of potassium hydroxide required to neutralize the acidic constituents in one gram of material. The determination is usually performed by titrating a solution of the substance with 0.1 N alkali to an end point of pH 8.7. The acid number determination is used mainly in the analysis of animal and vegetable oils, fats, and waxes and, to a lesser extent, petroleum oils and waxes. Also, products derived from these substances, such as soaps, paints, fuels, coatings, and lubricants are sometimes evaluated in terms of acid numbers.

The acidity of animal and vegetable oils, fats and waxes is due almost entirely to the presence of free fatty acids, which are produced in the substance by the hydrolysis of the constituent gly-

cerides. The hydrolysis may be caused by chemical treatment, enzymatic action, or bacterial decomposition. Therefore, the acid number of natural oils and fats is a variable property, which is related to conditions of manufacture, age and storage. Fresh vegetable oils seem to contain small percentages of free fatty acids, whereas animal fats in the fresh state are practically devoid of them. Generally, in fats of good quality, the amount of free fatty acids is not ordinarily greater than about 1 per cent, although in fats obtained from damaged materials it may be much higher. Palm oil and inedible tallow and greases are characteristically high in free fatty acids, ranging from 3 to 30 per cent. Thus, the importance of the acid number lies in the fact that it indicates the quality of a fatty substance. Certain arbitrary limits have been established for fats and oils in good condition. The range of values frequently reported in the literature is: butter fat, 0.45-2.0; coconut oil, 2.5-10.0; corn oil, 1.4-2.0; cottonseed oil, 0.6-0.9; lard, 0.5-0.8; menhaden oil, 5.0-8.0; mutton tallow, 1.7-14.0; olive oil, 0.3-1.0; rape oil, 0.4-1.0; and soya oil, 0.3-1.8.

The acidity of fats frequently is expressed directly as percentage free fatty acids. In these calculations, the assumption is made that the free fatty acids in the substance have a molecular weight equal to a specific fatty acid. For example, the free fatty acids (F.F.A.) are calculated as lauric acid for coconut and palm kernel oils, as palmitic acid for palm oil, as ricinoleic acid for castor oil; and as oleic acid for most other oils. One unit of acid number is equivalent to 0.357 per cent F.F.A. as lauric acid; 0.456 per cent F.F.A. as palmitic acid, 0.531 per cent F.F.A. as ricinoleic acid; and 0.503 per cent F.F.A. as oleic acid.

The scope of the acid number determination, as designed for petroleum products and lubricants, has been extended to include as acidic constituents: organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, and addition agents such as inhibitors and detergents. A set of standards on petroleum products specifies maximum allowable acid numbers for the following lubricating oils: general use oil (medium grades), 0.10-0.30; steam cylinder oil, 0.80; and diesel and marine engine oils, 3.00. The acid number may be used to express changes that occur in a lubricating oil used under oxidizing conditions. However, the acid number cannot be used to predict the performance of an oil under service conditions.

C. C. CHAPPELLOW JR.

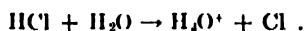
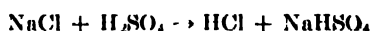
Cross-references: *Acids, Fats, Fatty Acids, Glycerides, Vegetable Oils, Waxes*

ACIDS

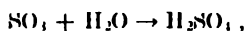
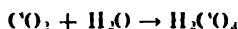
Acids comprise a group of organic or inorganic compounds which in water solution taste sour, liberate hydrogen when they react with metals, neutralize alkaline compounds, change the color of litmus indicator from blue to red, make characteristic changes in the colors of other indicators,

and have pH value less than 7. Considered from a broader standpoint, any compound that is a proton donor is an acid. With solvents other than water, the proton donor definition is fruitful. In water solution, however, acids are generally considered to be compounds capable of producing hydrogen or, better, hydronium (H_3O^+ or $\text{H}\cdot\text{H}_2\text{O}^+$) ions.

There are well over 100 kinds of acids that are commercially available. They are prepared in several ways: (1) By the reaction of a salt with an acid of a higher boiling point than the acid sought. For example, sulfuric acid has a high boiling point and it is stable. It reacts with chlorides to liberate hydrogen chloride which has a lower boiling point than sulfuric acid. Hydrogen chloride dissolved in water forms hydrochloric acid:



(2) The addition of water to an oxide, usually of a nonmetal (and called an acid anhydride):



(3) *Special methods:* Sulfuric acid is made by the chamber and the contact processes. Nitric acid is made by the catalytic oxidation of ammonia in the Ostwald process. Hydrogen chloride can also be made by direct combination of the elements. The gas is subsequently dissolved in water to form hydrochloric acid.

The *mineral acids* include sulfuric (H_2SO_4), hydrochloric (HCl), nitric (HNO_3), and phosphoric (H_3PO_4). Organic acids contain carbon, and usually contain the group or radical COOH , called the carboxyl radical. Such acids are *carboxylic acids*. Formic acid (HCOOH), acetic acid (CH_3COOH), and propionic acid ($\text{C}_2\text{H}_5\text{COOH}$) are in this group. Acids with a larger number of carbon atoms such as palmitic ($\text{C}_{15}\text{H}_{31}\text{COOH}$) and stearic ($\text{C}_{17}\text{H}_{33}\text{COOH}$), are acids that may be derived from fats and oils. Hence this entire group of carboxylic acids is called the *fatty acids*. Some monocarboxylic acids may be unsaturated such as acrylic (or propenoic) acid ($\text{CH}_2=\text{CHCOOH}$) and oleic acid ($\text{C}_{17}\text{H}_{31}\text{COOH}$).

Dicarboxylic acids contain two carboxyl groups. The simplest is oxalic acid ($\text{COOH}\cdot\text{COOH}$), a white solid, melting point 189°C as the dihydrate $[(\text{COOH})_2\cdot 2\text{H}_2\text{O}]$. This compound might also be called ethanedioic acid. Propanedioic acid, better known as malonic acid ($\text{COOHCH}_2\text{COOH}$), m.p. 135.6°C , is also in this group.

Aromatic carboxylic acids include benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$), found in cranberries. It is used as a preservative for foods. Its sodium salt, sodium benzoate, is sometimes used to preserve fruit juices and tomato ketchup.

Three phthalic acids are known, of which the ortho- is the most important. It is $\text{C}_6\text{H}_4(\text{COOH})_2$, 1,2-benzenedicarboxylic acid, m.p. $206\text{--}208^\circ\text{C}$. Its anhydride, phthalic anhydride $[\text{C}_8\text{H}_4(\text{CO})_2\text{O}]$, is used to polymerize with glycerol to form a useful resin.

Phenol, sometimes called carboic acid, ($\text{C}_6\text{H}_5\text{OH}$), is an organic acid that reacts with sodium hydroxide, a typical base, to form sodium phenoxide (or sodium phenolate) and water. $\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O}$. In contrast to carboxylic acids, phenols in general do not react with sodium hydrogen carbonate (bicarbonate of soda) (NaHCO_3), but many carboxylic acids do.

Amino acids are a group of 21 nitrogen-containing acids that may be derived from the decomposition of complex proteins. They all contain at least one carboxyl group.

Strong acids are those that are completely dissociated into ions in water solution. Weak acids show small tendency to form ions. For example, the reaction $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$ goes practically to completion when hydrochloric acid, a strong acid, is formed. Acetic acid solution $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$ forms only a few ions, and its properties are those of a weak acid. In this sense, glacial acetic acid is even weaker than a solution of hydrogen acetate in water. Concentrated sulfuric acid is weak and dilute sulfuric acid is strong.

The dissociation of the first hydronium ion from an acid in general proceeds more readily than a second. For example, $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$ is easier than $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$, and far easier than $\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{PO}_4^{3-}$.

The dissociation constant (or ionization constant) for an acid is a measure of the extent to which it forms hydrogen (or hydronium) (H^+ or H_3O^+) ions in water solution. In the case of acetic acid

$$\frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5}$$

This dissociation constant has a larger value for strong acids than for weak ones. In cases in which an acid dissociates more than one hydrogen (hydronium) ion, the value for K_1 for the second hydrogen ion is always smaller than that for the first.

ELBERT C. WEAVER

Cross-references: *Acid Number, Amino Acids, Carboxylic Acids, Anhydrides, Acids (Mineral), Fatty Acids, Ions*

ACIDS, MINERAL

Sulfuric Acid

The mineral acids are sulfuric acid, nitric acid, mixed acid, hydrochloric, hydrobromic and hydrofluoric acids, phosphoric acid, and boric acid. They are called mineral acids to indicate that they are derived from minerals, in contrast to the organic acids which are found in vegetable and animal matter.

Sulfuric acid is the most important of the mineral acids, as shown by the production figures. One reason is that it is relatively cheap; the overall figure for sulfuric acid sold in 1952 was about \$17 a ton (in terms of 100% H_2SO_4); another is that by adding sulfuric acid to the salts of the

other acids, the latter may be regenerated. Sulfuric acid, on the other hand, is not liberated from its salts by other acids; upon heating, the other acids volatilize, leaving the sulfates unaffected. With higher heat, the sulfates decompose. A third reason for the extensive use of sulfuric acid is its avidity for water; a fourth is its catalyzing properties. It functions in still other ways, one of which is in the neutralization of alkalies.

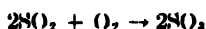
Sulfuric acid near the 100 per cent strength is an oily liquid, with strong corrosive properties. It is miscible with water in all proportions. In slight dilution, it freezes easily, well above the ice point. At greater dilutions, it may be cooled to minus 10°C and lower without freezing. Distinct from the 100% strength are the *Oleums*, which contain an excess of sulfur trioxide, and are made in a number of strengths; their freezing point curve also has peaks and valleys, but in the main, they freeze or solidify more easily.

The production figures for various mineral acids for 1952 are as follows (in short tons)

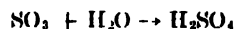
Sulfuric acid as 100% H_2SO_4	13,308,558
Nitric acid as 100% HNO_3	1,639,014
Mixed acid	142,745
Hydrochloric acid as 100% HCl	683,742
Hydrofluoric acid as 100% HF	41,512
Phosphoric acid as 50% H_3PO_4	2,061,099
Boric acid as 100% H_3BO_3	54,548

Sulfuric acid is made from sulfur (brimstone) or pyrite, by combustion, as a result of which sulfur dioxide is formed, more or less diluted by air. The acid may be made from any mixture of sulfur dioxide and air, as for example from copper blast furnace gas. The acid is made by one of two methods: the chamber process, or the contact process. The chamber process is the older. In its original lay-out, the gas from the sulfur or pyrite burner was passed into a series of lead chambers, along with air, nitric oxide gases and either atomized water or steam, the mixture of gases passing from one to the next. The reaction was slow, the temperature of the gases within the chambers rising to not more than 110°F. The reaction evolves heat, which is removed by air-cooling through the lead walls. There collects on the bottom of the chambers, particularly the first one, a sulfuric acid of 50°Bé, which is just the right strength for making superphosphate, a chemical fertilizer. The outgoing gases are scrubbed in strong sulfuric acid to recapture the nitric oxides, which are used over again. The present day chambers are far smaller than the original ones, the temperature at which they function is higher (about 225°F in the first chamber), and the chemical action is far more rapid. The chambers are often built outdoors, and some, whether inside or out, are water-cooled. There are still other modifications of the chamber process.

The second method is the contact process, in which the sulfur dioxide-air mixture travels at a measured rate over and through beds of pellets of a solid catalyst at a regulated, but elevated temperature. The first product is sulfur trioxide.



The solid contact substance first employed was finely divided platinum carried on asbestos fibers; it required a complete cleaning and drying of the gas, because the contact substance was easily poisoned, and its efficiency reduced. The pellets used more and more today, are vanadium pentoxide, on an inert carrier; they are less sensitive to impurities in the gas. The sulfur trioxide combines with water to form sulfuric acid,



but it does so explosively, it is therefore customary to dissolve the sulfur trioxide in concentrated sulfuric acid, in which it dissolves quietly yet completely, and to adjust the strength later.

The production of chamber acid in 1952 was 2,709,279 short tons, while that of the contact acid was 10,599,279 tons. From the 100 per cent chamber acid production before 1900, it has gradually decreased, passing the 50 per cent mark in 1938, while now the chamber acid production is only 20.3 per cent of the total. All acid figures are on the basis of 100 per cent H_2SO_4 .

Sulfuric acid, sometimes called the work horse of industry, has hundreds of uses. One of them is "battery acid", of specific gravity 1.250, which every motorist carries in his lead storage battery. For comparison, 100 per cent sulfuric acid has a specific gravity of 1.8305 at 20°C. Some other of its many uses are indicated below for 1951.

	Short tons
Fertilizers	
Superphosphate of calcium	3,950,000
Ammonium sulfate	1,500,000
Chemicals	3,900,000
Petroleum refining	1,550,000
Rayon and film	710,000
Iron and steel	1,090,000
Other metals	200,000
Explosives	115,000
Textiles	40,000
Miscellaneous	395,000

Nitric Acid

Nitric acid is made by the action of sulfuric acid on sodium nitrate, originally from Chile; there is formed nitre cake, or sodium acid sulfate as a second product, and concentrated nitric acid, over 95 per cent.



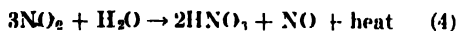
Chilean nitrate is still in use, and is in part the source of nitric acid in certain countries. There is, however, a new method, which takes its nitrogen from the air and makes it into nitric acid, after first combining it with hydrogen. In other words, the new method is the catalytic oxidation of synthetic ammonia.



The catalyst is a multiple screen of fine platinum wire held at red-hot heat by good insulation. The nitric oxide becomes dioxide on leaving the converter, reacting with the excess air present.

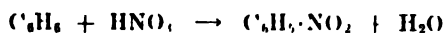


The nitrogen dioxide passes to a series of absorption towers where it travels countercurrent to a flow of weak acid, which increases in strength in each tower.



The nitric oxide reformed is oxidized again in the towers, so that finally almost all of it is absorbed. The acid discharged is 55 to 60 per cent HNO_3 .

The main use of nitric acid is in nitrations, such as that of benzene



The nitration is usually performed with mixed acid, and the function of the sulfuric acid is to absorb the water of reaction, which otherwise would slow down the rate of nitration and finally prevent it altogether. Ethylene glycol, glycerine and cellulose are other substances which may be nitrated. Nitric acid is more expensive than sulfuric acid; the average figure for the acid on the basis of 100% acid in 1952 was \$70 a ton (See Nitration)

Hydrochloric Acid

Hydrochloric acid is the water solution of hydrogen chloride, HCl , and is generally referred to by that symbol. Its most common form is the 20°Bé strength, with 31.45 per cent HCl . In recent years, a certain amount of the anhydrous substance has been prepared, bottled (in steel bottles) and shipped to customers.

Hydrochloric acid is the acid of which common salt, NaCl , is the sodium salt. It is made by one of three methods.

(1) By the action of sulfuric acid on salt; on heating, the hydrogen chloride and such water as may be present pass over to the absorption vessel and towers, there to meet countercurrently a weak solution of the acid or water. The reaction between nitre cake and salt, already given in this division produces hydrochloric acid and salt, in the mechanical salt cake furnace. In at least one large scale operation, a stream of sulfuric acid itself is allowed to flow on a mass of salt cake to which salt is constantly added, in a Mannheim furnace, but the general practice is to use nitre cake wherever possible.

(2) By burning chlorine from an electrolytic cell in an excess of hydrogen, and dissolving the resulting hydrogen chloride in water. A mixture of hydrogen and chlorine in certain proportions is violently explosive, so that careful regulation is essential.

(3) By salvaging and dissolving in weak acid or water the by-product hydrogen chloride formed in the chlorination of hydrocarbons.



The overall price at the factory of the three types of hydrochloric acid differs. The acid from salt, on a 100 per cent basis, is \$82.50; that from chlorine burned in hydrogen, \$78; while the acid obtained as by-product, is \$50 a ton.

Hydrofluoric Acid

Hydrogen fluoride is a gas, extremely soluble in water; the solution is called hydrofluoric acid. Hydrogen fluoride is liberated from its calcium salt by the action of concentrated sulfuric acid on the finely powdered mineral fluorspar, CaF_2 . Hydrofluoric acid attacks silicates of any kind; with silica SiO_2 , it forms silicon tetrafluoride. The acid is shipped in 30 per cent or 60 per cent HF strengths, in lead bottles. It serves for making the soluble fluorides, for preparing glass-etching and glass-brightening baths, and for cleaning stone. The anhydrous acid is also prepared commercially, and is used for the alkylation of hydrocarbons in petroleum refineries.

Phosphoric Acid

Phosphoric acid is a liquid; it is prepared by the wet or the dry method. In the wet process, diluted sulfuric acid is allowed to act on calcium phosphate in the form of ground phosphate rock or bone ash. There is produced a first strength of 40% phosphoric acid, which may be concentrated somewhat further. The concentrated grades are generally made by the second method, which produces yellow phosphorus as a first product. The phosphorus is oxidized to phosphorus pentoxide—a white, extremely hygroscopic solid, from which any strength acid is made. In this second process, a charge of calcium phosphate rock, carbon and silica, is fed into the electric furnace; phosphorus is evolved in vapor form, and may be collected directly. The liquid first formed solidifies easily and may be kept under a blanket of water. Shipments in specially equipped car tanks are made, with this protection.

It is used to make the sodium phosphates, calcium phosphate and other phosphates; to produce double and triple phosphates, which are double and triple strength because no inert calcium sulfate remains in the product, as is the case when sulfuric acid is used; to substitute for tartaric and citric acid in preserves and soft drinks; to manufacture pharmaceutical chemicals and dental cements. It is used as a clarifying agent in the sugar house; in water softening; as a drying agent, and in numerous other industrial operations and preparations.

Boric Acid

Boric acid, H_3BO_3 , is made by treating borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, with sulfuric acid. It is a solid, and may be obtained as a very fine, air-borne powder, as a granular powder, or in the form of crystals. It is made in a technical grade, and a U.S.P. grade. The U.S.P. grade is a pharmaceutical: its saturated solution is a mild antiseptic, or at least, a bacteriostatic agent. The technical grade finds use in ceramics, and in other industries. Borax is obtained from the brine in Searles Lake, but very especially from rasorite, a mineral, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$; the latter gives by solution, filtration and recrystallization, the desired borax.

E. R. RIEGEL

Cross-references: Acids, Nitration, Nitrates, Fertilizers

ACRYLIC RESINS

Acrylic resins comprise monomers and polymers of acrylic, substituted acrylic and methacrylic acids, their salts, esters and other derivatives, such as nitriles and amides. Classified by major chemical types, the acrylics resins may be grouped as follows:

Acid Monomers and Polymers. *Acrylic acid* $\text{CH}_2=\text{CHCOOH}$, is a corrosive, weak acid, available in either aqueous solution or as a glacial (essentially anhydrous) form. Reactions of acrylic acid are typical of normal acid functions (ester and salt, anhydride and acid chloride formation), of the unsaturated function (addition of halogens, amines, mercaptans), and of the conjugated functions (Diels Alder reaction). All reactions are qualified by the polymerizable nature of the molecule. *Polyacrylic acid*, available as an aqueous solution in different viscosities and as an anhydrous powder, is a water-soluble polymer which gives hard, brittle, clear films. It is capable of undergoing chemical reactions involving the acid function, such as salt formation and esterification, insolubilization being achieved in the latter instance by the use of polyfunctional alcohols. *Methacrylic acid*, available in anhydrous form, is similarly amenable to reaction of the two function groupings in the molecule as well as to polymerization.

Salts. Monomeric salts may be prepared by neutralization of the corresponding acid or by suitable saponification of the appropriate monomeric ester. Polymeric acrylic salts may be prepared by (a) neutralization of the polymeric acids, (b) polymerization of the monomeric salts, (c) saponification of the polymeric acrylic esters, and (d) saponification of the polymeric nitrile.

Esters. A wide range of monomeric acrylic esters is available, and large quantities of methyl and ethyl acrylates and methyl methacrylate now are being produced. These are capable of undergoing reactions of the ester grouping, and of the unsaturated system present in the molecule, including polymerization.

The polymeric esters may be considered from the point of view of four methods of polymerization. (1) The monomeric esters can be polymerized in bulk by casting techniques to give sheet materials. Acrylic resin sheet based principally on methyl methacrylate is a hard, transparent, optically clear product with excellent resistance to water and some organic solvents. (2) Suspension polymerization of the monomeric esters has been used to prepare commercial molding powders such as "Lucite" and "Plexiglas." (3) Polymerization of acrylic esters in organic solvents. A large range of solvents has been used for the preparation of soluble polymers, the properties of which permit application in coating, adhesive and lubricating oil compositions. (4) Emulsion polymerization techniques. These stable dispersions of discrete particles of acrylic polymers form films on drying.

Nitriles. Acrylonitrile monomer ($\text{CH}_2=\text{CH}-\text{CN}$) is a liquid capable of ready polymerization and is reactive due to its carbon-to-carbon unsaturation and its nitrile function. Polymeriza-

tion, which may be carried out in aqueous suspension or in solution, provides the basic material for the preparation of such synthetic fibers as "Orlon," "Acrilan," "Dynel" and others. Polyacrylonitrile is soluble in dimethylformamide, ethylene carbonate, tetramethylene sulfone, and aqueous solutions of thiocyanate salts. It may be formed into fibers by extruding a polymer solution into a coagulating bath or by dry spinning. Hydrolyzed polyacrylonitrile has aroused interest as a modifier of soil structures. Copolymers of acrylonitrile and other monomers, such as styrene and butadiene, are numerous and are characterized by numerous useful properties.

Sheets and Molding Powders. The properties exhibited by solid polymers such as crystal clarity, high impact strength, resistance to sunlight, weather, many chemicals, and formability—have led to their widespread use in military and commercial applications. Availability of the material in translucent, transparent and opaque colors has expanded and diversified applications.

Sheet acrylic polymer is the standard material for transparent enclosures on aircraft. Large edged sheets are used as radar plotting boards on shipboard and at ground control stations. New grades of acrylic having improved resistance to heat and crazing have been developed for jet aircraft. In the field of merchandising, acrylic plastic has become a major sign material, particularly for outdoor use. It also is used for counter dividers, transparent demonstration models of household appliances and industrial machines, and display fixtures and cases. The ability of acrylic resin to resist breakage and corrosion and to transmit and diffuse light efficiently makes it advantageous for industrial window glazing, dome skylights, safety shields, inspection windows, machine covers, pump components and plating barrels.

In molding powder form, acrylic plastic is used extensively for automotive parts such as tail and stop light lenses, steering wheel medallions, nameplates and instrument panels. A recent style trend introduced transparent roof sections formed from acrylic sheet. The beauty and durability of molded acrylic parts have resulted in wide use for nameplates, control knobs, dials and handles on all types of home appliances, and many miscellaneous items.

Ion Exchange Resins. Cation exchange resins may be produced by the polymerization of methacrylic acid in the presence of crosslinking agents such as divinyl benzene.

Textiles. Blends of polyacrylonitrile fibers with those of wool, rayon and acetate provide a means of obtaining mixed fibers with dyeing and other properties characteristic of the fiber types present in the blend. Acrylic resins are well established in the sizing of fibers, polyacrylic acid being used extensively in the nylon field. Acrylate dispersions provide highly desirable types of finishes.

Coatings. Acrylic resin emulsion paints constitute a recent major development. They are especially recommended for freedom from odor, durability of finish, speed of drying and ease of application. For application either by spraying

or brushing, acrylic resin coating solutions in organic solvents are available in types which give almost any desired range of hardness or tackiness, with clarity and durability as prominent features. These coatings are for both decorative and protective uses, ranging from the protection of art treasures to treatment of raincoats.

Leather. Acrylate dispersions are used in leather finishing as a base coat for nitrocellulose finishes and as components of water finish systems.

Oil Additives. Polymerized acrylic esters, along with polyisobutylene and alkylated polystyrene, find some use as viscosity index improvers for hydraulic oils, automatic transmission fluids and motor oils. Methacrylate esters are used as pour point depressants for waxy oil stocks.

Cross-references: *Diels-Alder Reaction, Esters, Monomers, Polymerization, Nitriles, Plastics, Ion Exchange, Protective Coatings, Fibers (Synthetic)*

ACTINIDES *see* TRANSURANIUM ELEMENTS

ACTIVATED CARBON, *see* CARBON, ACTIVATED

ACTIVATED SLUDGE

Activated sludge is the biologically active sediment produced by the repeated aeration and settling of sewage and/or organic wastes. The dissolved organic matter acts as food for the growth of an aerobic flora. This flora produces a biologically active sludge which is usually brown in color and which destroys the polluting organic matter in the sewage and waste. The process is known as the activated sludge process.

The activated sludge process, with minor variations, consists of aeration through submerged porous diffusers or by mechanical surface agitation, of either raw or settled sewage for a period of 2-6 hours, followed by settling of the solids for a period of 1-2 hours. These solids, which are made up of the solids in the sewage and the biological growths which develop, are returned to the sewage flowing into the aeration tanks. As this cycle is repeated, the aerobic organisms in the sludge develop until there is 1000-3000 ppm of suspended sludge in the aeration liquor. After a while more of the active sludge is developed than is needed to purify the incoming sewage, and this excess is withdrawn from the process and either dried for fertilizer or digested anaerobically with raw sewage sludge. This anaerobic digestion produces a gas consisting of approximately 65% methane and 35% CO_2 , and changes the water binding properties so that the sludge is easier to filter or dry.

The activated sludge is made up of a mixture of zoogeal bacteria, filamentous bacteria, protozoa, rotifera and miscellaneous higher forms of life. The types and numbers of the various organisms will vary with the types of food present and with the length of the aeration period. The settled sludge withdrawn from the process contains from 0.6 to 1.5% dry solids, although by further settling it may be concentrated to 3-6% solids. Analysis of

the dried sludge for the usual fertilizer constituents show that it contains 5-6% of slowly available N and 2-3% of P. The fertilizing value appears to be greater than the analysis would indicate, thus suggesting that it contains beneficial trace elements and growth-promoting compounds. Recent developments indicate that the sludge is a valuable source of vitamin B_{12} , either by extraction of the B_{12} or for direct addition of the dried sludge to mixed foods for cattle and poultry.

The quality of excess activated sludge produced will vary with the food and the extent of oxidation to which the process is carried. In general, about 1 lb of sludge is produced for each lb of organic matter destroyed. Prolonged or over-aeration will cause the sludge to partially disperse and digest itself. The amount of air or more precisely oxygen that is necessary to keep the sludge in an active and aerobic condition depends on the oxygen demand of the sludge organisms, the quantity of active sludge, and the amount of food to be utilized. Given sufficient food and sufficient organisms to eat the food, the process seems to be limited only by the rate at which oxygen or air can be dissolved into the mixed liquor. This rate depends on the oxygen deficit, turbulence, bubble size and temperature, and at present is restricted by the physical methods of forcing the air through the diffuser tubers and/or mechanical agitation.

In practice, the excess activated sludge is conditioned with 3-6% FeCl_3 and filtered on vacuum filters. This reduces the moisture to about 80% and produces a filter cake which is dried in rotary or spray driers to a moisture content of less than 5%. It is bagged and sold direct as a fertilizer, or to fertilizer manufacturers who use it in mixed fertilizer.

The mechanism of purification of sewage by the activated sludge is two fold i.e., (1) absorption of colloidal and soluble organic matter on the floc with subsequent oxidation by the organisms, and (2) chemical splitting and oxidation of the soluble carbohydrates and proteins to CO_2 , H_2O , NH_3 , NO_2 , NO_3 , SO_4 , PO_4 and humus. The process of digestion proceeds by hydrolysis, decarboxylation, deamination and splitting of S and P from the organic molecules before oxidation.

The process is applicable to the treatment of almost any type of organic waste waters which can serve as food for biological growth. It has been applied to cannery wastes, milk products wastes, corn products wastes and even phenolic wastes. In the treatment of phenolic wastes a special flora is developed which thrives on phenol as food.

W. D. HATFIELD

Cross-references: *Fertilizers*

ACTIVITY

The term "activity" is used in a general way to refer to the rate or extent of a change associated with some substance or system. Thus the activity of magnesium metal is greater than that of copper, for it will combine more rapidly and to a larger extent with a variety of substances and will displace copper from many of its compounds. This

general meaning is also implied when activity is used in words or phrases like radioactivity, optical activity, catalytic activity and biological activity.

Activity has a more specialized meaning in chemical thermodynamics. The behavior of ideal systems at equilibrium is described by laws which are relations involving the concentrations of the species present. The substitution of activities for concentrations, as suggested by G. N. Lewis, preserves the mathematical form of the ideal law and enables it to be extended to real systems, particularly liquid solutions and alloys. For example, the ratio of the product of the activities of hydrogen and acetate ions to the activity of un-ionized acetic acid has a fixed value independent of the concentration of acid or the presence of salts, whereas the ideal mass action constant, which is the ratio of concentrations, is not strictly constant. The activity of a chemical species can be expressed as the product of its concentration and an activity coefficient that measures the deviation of the species from ideal behavior. The numerical value of the activity and activity coefficient will depend upon the unit of concentration employed. For electrolytes the mean activity (a_{\pm}) and mean activity coefficient are used because the activity and activity coefficient of a single ionic species cannot be measured and can thus be used only in a formal way. The relation between mean and ionic activities is illustrated by $a_{\pm} = (a_{\text{H}^+} \cdot a_{\text{C}_2\text{H}_3\text{O}_2})^{1/2}$ for potassium chloride and $a_{\pm} = (a_{\text{Na}^+} \cdot a_{\text{Cl}^-})^{1/2}$ for barium chloride.

Activity coefficients and activities are most commonly obtained from measurements of vapor pressure lowering, freezing point depression, boiling point elevation, solubility, and electromotive force. In certain cases they can also be estimated theoretically. As commonly used, activity is a relative quantity having unit value in some chosen standard state. Thus the standard state of unit activity for water in aqueous solutions of potassium chloride is pure liquid water at 1 atm. pressure and the given temperature. The standard state for the activity of a solute like potassium chloride is often so defined as to make the ratio of the activity to the concentration of solute approach unity as the concentration decreases to zero.

The relative nature of activity is shown also by its formal definition as the ratio of the fugacity of the substance in the given state to its fugacity in the standard state or by its relation to the chemical potentials (μ and μ^0) of the substance in the given and standard states: $\mu = \mu^0 + RT \ln a$ (R is the gas constant and T the absolute temperature). An absolute activity (λ) can be defined by $\mu = RT \ln \lambda$, but this has not come into general use. The variation of the activity of a species i with temperature is related to its relative partial molal heat content (L_i) by $(\partial \ln a_i / \partial T)_{P,N} = (L_i / RT^2)$. The influence of total pressure on activity is given by $(\partial \ln a_i / \partial P)_{T,N} = V_i / RT$ where V_i is the partial molal volume of the species.

EDWARD J. KING

Cross-references: *Electromotive Series, Solutions, Ions, Coefficients, Debye-Huckel Theory*

ADDITIVES

The term "additive" has come into general use in recent years as an inclusive name for a wide range of chemical substances which are added to various types of end products, usually in rather low percentage, to provide some unique property or to stabilize them against spoilage or deterioration. Though in a broad sense it could be interpreted to mean "anything that is added" to a base substance (such as fillers, pigments, reinforcing agents, diluents, etc.), it properly refers to special-purpose ingredients, such as antioxidants in rubber; degumming agents in gasoline; viscosity index improvers and pour point depressants in lubricating oils; fortifying ingredients (vitamins) in wheat flour; mold inhibitors, emulsifiers, protective colloids, preservatives and other types of stabilizer in miscellaneous food products. An exhaustive list of additives used in foods is given in the chapter by C. N. Frey in Blum's "Handbook of Food and Agriculture." Perhaps the most widely known and used "additive" is tetraethyl lead in high octane gasoline to reduce engine knock, or detonation of the gas-air mixture in the cylinder head; less than one part in 1,000 parts of gasoline is sufficient. Methacrylate esters and acrylic esters are added in small proportions to engine oils to help maintain proper viscosity. Similarly, the use of only 0.25 per cent of phenylbetanaphthylamine is sufficient to retard greatly the oxidation of vulcanized rubber.

"Additive" is a vague and not particularly useful term, as it is so general as to be practically meaningless until properly qualified. The practice of using low percentages of antioxidants, stabilizers and other preservatives had been in existence for many years before this word became current. Though it is not precise, it probably serves some purpose as a convenient general word to include the substances and uses mentioned above. However, it might be preferable to use the functional name wherever possible, i.e., antioxidant, preservative, mold-inhibitor, anti-knock agent.

G. G. HAWLEY

Cross-references: *Lubricating Oils, Foods, Gasoline*

ADHESIVES

Adhesives are substances used to bond or stick together two or more layers or units of other materials. Several basic mechanisms explain this bonding action. In some instances, there is evidence that chemical bonds are established involving electron sharing, though more usually mechanical considerations prevail. Mechanically, adhesives may depend upon a rough surface or a highly tacky adhesive demonstrating good resistance to high rates of shear. Whether the adhesive bond is due to chemical or mechanical bond or a combination of both, high bond strength is also predicated upon high cohesive strength in the adhesive film—in particular to the innate properties of the adhesive material. Thus the evolution of adhesives has paralleled the developments of film-forming materials, notably those

which are classified as plastics materials. This includes high polymers of natural or synthetic origin. A review of how films are formed explains in part how adhesives cure or set.

(1) *Evaporation of volatiles.* Thermoplastic high polymers, in particular, where chain length has previously been established, form films on solvent evaporation. Good adhesive bonds require solvent evaporation before assembly or through one of the adherends, which must be porous. As solvents are evaporated, latent catalysts may become effective and cross-link. Some polymers (rubber adhesives) rely on heat to effect complete cure.

(2) *Volatiles diffuse into porous adherend.* Some adhesive formulations with solvents or matrices which possess high boiling points may bond on the diffusion of this volatile into a porous adherend. Aqueous dispersions or water solutions of adhesives develop good bonds in this manner. For example, sodium silicate solutions bond paper boxes effectively on the rapid diffusion of water into the porous paper stocks.

(3) *Polymerization processes form films.* Many synthetic resin adhesives form good adhesive films as they cure in the presence of curing agents which catalyze or cross link the structure: epoxy resins, polyesters, furanes, phenolics, ureas, and most thermosetting polymers. Bonds to nonporous adherends are most effective, particularly if polymerization proceeds without formation of volatile by-products. Final cure and good adhesive strength depend in many instances upon the application of heat. Pressure is important only insofar as it keeps adherends in close juxtaposition during cure and prevents formation of voids.

Forms. As the adhesive is offered to industrial users, it may appear in various physical forms, including all necessary additives to make a good adhesive: (a) powders, which may be melted or dissolved; (b) solutions of film-forming materials; (c) dispersions of film formers (as rubber latices); (d) supported (reinforced) or nonsupported films; (e) meltable stocks or rods; (f) separate packages of resin compounds and curing agents.

Phenol-Formaldehyde Resins. One of the first successful synthetic resin adhesive groups to achieve industrial prominence, phenolics are fulfilling many applications. Luting compounds for electric light bulbs; bonding agents for grinding wheels; hot set, and waterproof adhesive for plywood are a few examples. Resorcinol-formaldehyde has been singularly successful in bonding wood products.

Urea and Melamine Formaldehyde Resins. Both as resins and extenders for natural polymers, urea and melamine formaldehyde adhesives have been singularly successful in the plywood industry. Extended with cellulosic fillers and mixed with water, they have proved useful as a general purpose adhesive for porous paper and wood products. Compounded with necessary curing agents they have cured to water-resistant bonds.

Epoxy Resins. Reaction products of epichlorohydrin and bisphenols, have offered some of the most outstanding adhesives. With very low shrink-

age during cure and excellent stability, they have demonstrated their quality in bonding glass, metals, and ceramics better than other adhesives. Blended with certain phenolics, they have outstanding bond strength at high temperatures. As pastes and laminating agents they are widely used to repair metal and concrete structures.

Polyesters. As adhesives for laminated polyesters and as patching compounds for some ceramics, polyester adhesives enjoy limited fields of applications. However, in combination with diisocyanates which can react on available hydroxyl groups, a promising group of adhesives exists.

Polyurethanes. Diisocyanates and polyols show promise as foaming agents as well as adhesives for wood and metal products. Up to now they have not been used extensively in the U.S.

Natural Rubber. Natural rubber, both as a latex and in solution form and compounded with appropriate curing agents, has long served as an adhesive for industrial rubber goods and for the fiber and metal reinforcement in automobile tires. Blended with natural resins (rosin and rosin esters, for example), it forms excellent pressure sensitive adhesives. General-purpose adhesives for a wide variety of products are based on rubber compounds.

Synthetic Rubbers. Chloroprene (neoprene) and copolymers of butadiene with styrene and with acrylonitrile serve as replacements for natural rubber adhesives and in addition provide some of the most outstanding metal bonding agents when modified with heat-curing phenolics. Both latices and solution forms are available. Rubber bonding agents are generally based on these materials and also find use in tile cements.

Furan Resins. Polymers based on furfuryl alcohol have found specialized widespread applications in several industries. As cements for acid-proof bricks they are a by-word in the chemical industries. As bonding agents for laminated phenolics and high-explosive compounds, they possess unique characteristics.

Asphaltic Compounds. Compounds based on asphalt modified with synthetic natural resins are low in cost and extensively used in large applications such as building construction (roofing compounds and sealants) and in setting floor tile.

Thiokol Compounds. Perhaps less valuable as an adhesive than as a sealant, "Thiokol" compounds will form waterproof bonds in metal tanks and containers and must always be considered in these fields.

Polyvinyl Acetate. Polyvinyl acetate emulsions have been recognized as outstanding thermoplastic adhesives for porous bodies, including wood. They are also used extensively as sprayed acoustic insulation cement, setting tiles, and in bonding miscellaneous materials where the water vehicle may be dissipated.

Shellac. Shellac has been useful as a laboratory repair adhesive, particularly in combination with rosin. Heat-meltable formulations are usually used.

Cellulose Nitrate. Many formulations find plasticized cellulose nitrate dissolved in solvents

TYPICAL INDUSTRIAL APPLICATIONS

Application	Suggested Adhesives
Plywood Interior Manufacture	Casein, Soybean Protein, Blood Albumin, Urea
Plywood Exterior Manufacture	Phenolic and Melamine
Bonds to Glass and Ceramics	Epoxies
Chemical Resistant Bricks	Furanes
Metal to Metal	Epoxies and Rubber Cements
Metal to Metal	Phenolic Modified Rubbers and Epoxies
Rubber to Metal	Rubber Cements and Some Epoxies
Paper Labels	Dextrins, Gum Arabic
Adhesive Tapes	Modified Rubbers, Polyisobutylenes
Asphalt and Rubber Floor Tiles	Asphaltic Compounds
Thermo-plastics to Themselves	Solvent Cements or Heat Welding where possible

to be useful as a repair cement. Household uses and a few industrial uses find celluloses valuable.

Animal Glue. The extraction of useful glues from the hide and bones of cattle has been practiced for many years. Wood and paper products still continued to be served by these materials.

Protein Compounds. Casein and soybean protein adhesives preceded the synthetic resin types and have proved useful on porous adherends. There is still considerable activity involving the use of these materials, particularly in soybean adhesives for plywood manufacture.

Gum Arabic and Gum Tragacanth. Long standbys as moistenable adhesives for paper labels, these natural resins are soluble in water.

Starch. The chemistry of starch has grown in recent years and today many types have adhesive uses, particularly on labels and paper products.

Sodium Silicates. Whether the bonding of core sands for foundries is involved or the adhesion of corrugated paperboard is necessary, sodium silicate adhesives find useful application.

Litharge-Glycerine. Pipe fittings bonded with litharge-glycerine pastes have been a favorite of plumbers for years. Ease of setting and permanent bonds are formed.

Hydrated Crystal Structures. Magnesium-oxychloride, Portland cement, and Keene's cement must be considered as another major group of inorganic bonding agents. Flooring cements, electrical insulating compounds, and grouting compounds rely on these inexpensive inorganics.

JOHN DELMONTE

Cross-references: *Plastics, Rubber, Binding Agents*

ADSORPTION

When any gas is brought in contact with any solid under the right conditions of temperature and pressure, the gas molecules are said to be

adsorbed on the surface of the solid. A common example is the adsorption of gases by activated charcoal. The solid is called the *adsorbent*; the adsorbed substance is called the *adsorbate*. Actually, either liquids or solids can act as adsorbents. Furthermore, adsorbates can be gases, liquids, solutes, or solvents. The most studied and best known examples of adsorption are gas-solid and liquid-solid systems. These will receive most attention in this discussion.

If the adsorbate molecules are held exclusively at the adsorbent interface, the process is called *adsorption*; if they penetrate into the interior of the adsorbent, the process is called *absorption*. In this connection the walls of capillaries, cracks and crevices in the solid are still considered as being part of the surface, (sometimes called the "inner surface"). Penetration into the actual lattice structure of the solid or into the interior of a liquid adsorbent must take place before the process is called *absorption* (See **Absorption**).

The picking up of a gas or liquid by an adsorbent is sometimes referred to as "sorption" when one does not wish to specify, or does not know whether a given process is adsorption or absorption.

Gas-Solid Adsorption. The adsorption of gases on solids has been found to fall into convenient classifications, known respectively as *physical* and *chemical* adsorption. Physical adsorption is so named because presumably it occurs through the operation of physical or van der Waals forces between the solid adsorbent and the adsorbate molecules. As one would expect, the extent of physical adsorption by a given solid will be related to the boiling point of the adsorbates rather than to the chemical nature of either the solid or the adsorbate. Chemical adsorption differs from physical adsorption in that it depends on chemical bond formation between the adsorbent and the adsorbate. Chemical adsorption is therefore highly specific. For example, the noble gases are not chemisorbed by any known solid because they cannot form adsorbate-adsorbent chemical bonds. Similarly, O_2 or N_2 at room temperature would not be expected to chemisorb on a relatively inert solid such as silica gel, but would be expected to chemisorb on reactive materials such as iron catalysts.

Physical Adsorption. The phenomenon of physical adsorption has been recognized for many years. However, because of the absence of any method for measuring surface areas, considerable confusion exists in much of the early work as to the thickness of the adsorbed layers. At the present time, with the help of new methods (See **BET Theory**) for measuring surface areas of solids, it is possible to state with fair certainty that physical adsorption may consist of monolayers, multilayers, or condensation of the adsorbate as a liquid in tiny capillaries of the adsorbent; indeed it may involve all three of these forms at one time. In all cases, however, it is well to keep in mind that physical adsorption is closely related to condensation in that it involves physical forces operating between the adsorbate mole-

cules and between the adsorbate and the adsorbent.

A survey of the literature a number of years ago indicated that all physical adsorption could be expressed by one of five types of adsorption isotherms or plots of the volume of gas adsorbed against pressure. These five isotherms types are shown in Figure 1. Type I is characteristic of physical adsorption of vapors in solids, the pores of which are so small as to prevent the building of layers thicker than a single layer. The adsorption of most vapors (particularly nonpolar) on charcoal yields isotherms of Type I. If the physical adsorption can build up indefinitely thick multilayers at sufficiently high relative pressures isotherms of Type II are obtained. These, have proved to be very useful (See BET Theory) for measuring surface areas of finely divided or porous solids by an adsorption method. If the heat of adsorption of a gas or vapor is less than the heat of liquefaction, isotherms of Type III are observed. The adsorption of water vapor on graphite or on de-oxygenated carbon black is of this type. If a solid has pores in a medium size range (20 to 500 Å in diameter, for example) they yield adsorption isotherms of Type IV, which presumably represent a combination of monolayer adsorption, multilayer adsorption and capillary condensation. Silica alumina catalysts of the type used for cracking hydrocarbons to form gasoline usually yield this type of isotherm. Finally, if the heat of adsorption is small, solids having small pores will yield isotherms of Type V. This can be illustrated by curves for the adsorption of water vapor on charcoal.

Space does not permit a detailed discussion of the thermodynamics of physical adsorption. It will perhaps suffice to point out two things. To begin with, since the adsorption of a gas on a solid involves a free energy decrease and an entropy decrease it follows that adsorption of a gas on a solid is always exothermic. Secondly, the isosteric heat of adsorption can be calculated from adsorption data by the Clausius Clapeyron equation

$$\ln \frac{p_2}{p_1} = \frac{\lambda}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where p_1 and p_2 are the adsorption pressures required to cause a given volume of gas to be adsorbed at temperatures T_1 and T_2 , respectively. For Types I, II, and IV isotherms the heat of adsorption is frequently 50 to 100% higher than the heat of liquefaction; whereas, for Types III and V it is equal to or less than the heat of liquefaction of the adsorbate.

One other factor related to the thermodynamics of physical adsorption should be mentioned. In the past it has seemed reasonable to base all derivations on the assumption that the solid itself is not influenced by the physical adsorption. But recent experiments by Yates have shown that the adsorption of certain gases such as nitrogen, argon, and krypton at -195°C on a sample of porous glass causes a considerable expansion, even for a small fraction of a monolayer of adsorbed gas on the glass. Other gases cause sharp

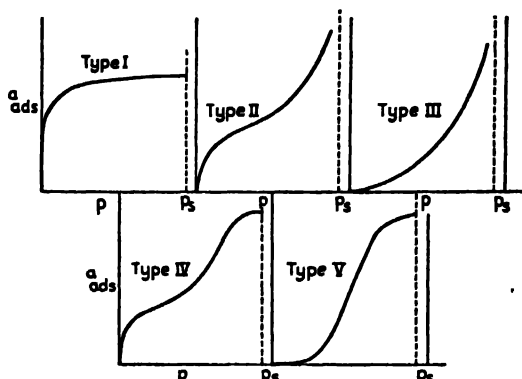


Fig. 1. Types of physical adsorption isotherms (taken from section on BET theory).

contraction with small coverages and expansion with large coverage. Clearly then, a detailed treatment of physical adsorption will have to include a consideration of changes both in the solid adsorbent and in the adsorbate.

The study of physical adsorption has received added attention since the discovery of evidence for the existence of multimolecular adsorption. S-shaped adsorption isotherms obtained, using N_2 as adsorbate and iron synthetic ammonia catalysts as adsorbents, seemed most easily interpretable as representing the building up of multilayers at the higher relative pressures. Actually, it appeared that the low pressure end of the long linear part of such an isotherm (designated as "Point B") corresponded to a statistical monolayer of adsorbed gas. This led in turn to the suggestion that one could calculate the area of a solid by merely multiplying the number of molecules adsorbed at Point B by a value for the cross-sectional area of the adsorbed nitrogen molecule (16.2 Å² is usually employed). A theoretical treatment of the S-shaped isotherms soon led to an equation known as the BET (Brunauer-Emmett-Teller) equation for obtaining the volume of gas in a monolayer and hence the surface area of the solid adsorbent (see BET Theory).

Capillary condensation, another component of physical adsorption, is of particular interest because of information it can give about pore size and pore size distribution of tiny capillaries in porous solids. The Kelvin equation

$$\ln \frac{p}{p_0} = \frac{2\sigma V \cos \theta}{rRT}$$

was derived in 1871 to show the relation between r , the radius of a capillary; p/p_0 , the relative pressure of the vapor in the capillary; T , the temperature; V , the molal volume of the adsorbate; σ the surface tension of the adsorbate, and θ the angle of wetting of the capillary by the liquid adsorbate. It expresses the fact that the pressure p above a liquid condensed in a capillary is less than the vapor pressure p_0 of the bulk liquid. Zsigmondy was the first to apply this equation to show the relation between capillary condensation and pore size. His calculations in-

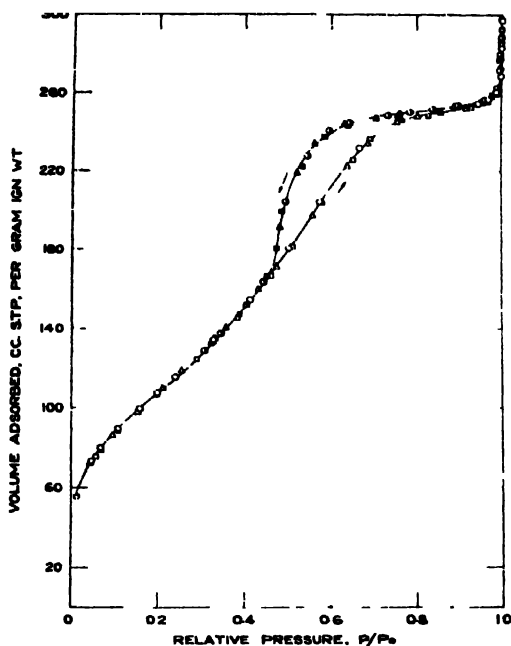


Fig. 2. Nitrogen adsorption-desorption isotherms for a silica alumina cracking catalyst as obtained by Ries and co-workers

volved a number of assumptions but were generally considered to furnish at least a semiquantitative estimate of pore size and distribution.

Soon after the existence of multimolecular adsorption was established, Wheeler called attention to the possibility of modifying the Kelvin equation in such a way as to improve the accuracy of pore size estimates. Specifically he recognized that the evaporation of capillary condensed liquid from a given pore at its equilibrium pressure p would leave a multilayer adsorbed on the capillary wall. The pore size calculated from the desorption curves of an adsorption-desorption isotherm such as is shown in Figure 2 would then give a capillary radius r smaller than the true radius r_0 by the thickness of the multilayer left on the walls. Methods have been worked out for taking multilayer adsorption into consideration and calculating from desorption isotherms the pore size and pore size distribution for capillaries in porous solids.

In summary then, one can say that new uses for physical adsorption have been found in the form of a new tool for measuring both the surface area of finely divided solids and the surface area, pore size, and pore size distribution of porous solids. In addition, it finds traditional use as the means by which adsorbents such as charcoal can be used in gas masks for removing poisonous gases from a stream of air or in commercial apparatus for solvent recovery and for air conditioning. Another rapidly growing use for physical adsorption is in the field of gas chromatography that is now being employed for analyzing a variety of gases.

Chemical Adsorption. Chemical adsorption partakes of most of the properties of chemical reactions. It occurs only under conditions in which on chemical grounds incipient bond formation between adsorbate and the adsorbent would be expected. It evolves an amount of heat that is usually in the range encountered in chemical reactions (5 to 100 kcal per mole of adsorbate in most cases). Furthermore, chemical adsorption is often slow and temperature sensitive. Energies of activation for chemical adsorption are frequently in the range 10 to 20 kcal per mole. Occasionally, however, chemical adsorption or chemisorption, as it is sometimes called, occurs instantaneously. This is true, for example, of the chemisorption of carbon monoxide on iron catalysts at -195°C . The heat of this adsorption is as high as 35 kcal per mole, but the energy of activation is so low as to be practically unmeasurable.

Multilayer chemisorption is, by definition, assumed not to exist. If an adsorbate is taken up chemically in quantities in excess of a monolayer, it is assumed to have reacted with at least some of the underlying layers of the solid and no longer represents chemisorption in the strictest sense of the word.

Although it is realized that an energy of activation is frequently involved in chemical adsorption, it is also recognized that extreme care must be used in calculating it. The difficulty can perhaps be best explained with the help of the adsorption isobar (a plot of the volume of gas adsorbed against temperature at constant pressure) for hydrogen on an iron catalyst promoted with Al_2O_3 and K_2O . Such a plot is shown in Figure 3. Types A and B are two different kinds of chemical adsorption of hydrogen. It is evident that any heat values obtained by applying the Clausius-Clapeyron equation to adsorption data taken partly from type A and partly from Type B would be of little significance. Only when the data are taken from isotherms for a single type of adsorption can calculated energies of activation be considered as even approximately correct. Actually, there is no assurance that only two types of chemisorption can exist between an adsorbate and a solid. Indeed, on iron catalysts promoted with Al_2O_3 , a

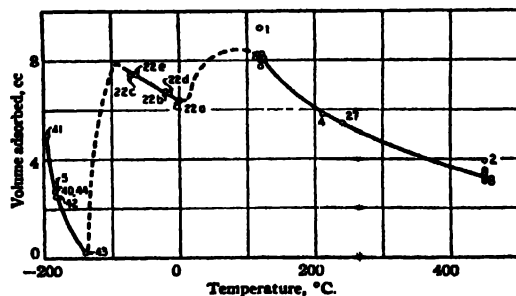


Fig. 3. Adsorption isobar for hydrogen on an $\text{Fe-K}_2\text{O-Al}_2\text{O}_3$ catalyst at a pressure of 1 atmosphere. The type of chemical adsorption extending from about -100° to 0°C is called "type A" adsorption; that occurring at and above about 100°C is called "type B" adsorption.



third type of chemical adsorption of hydrogen (called Type C) has recently been found to exist in the temperature range -100 to -195°C . Furthermore, there is ample evidence that chemical adsorption behaves as though the surface were heterogeneous. Originally it was suggested by Taylor that solid catalysts functioned through a number of "active centers" and that these active centers comprised a collection of surface atoms covering a wide range of energies of activation and heats of adsorption. Modern concepts suggest that these "active centers" may not actually represent fixed positions on a surface but may be continually created and destroyed as a result of electron motion within the solid attending the chemisorption of molecules on the surface. The difficulty therefore of calculating significant energies of activation or heats of adsorption for the chemical adsorption of gases on solid should be evident.

Chemical adsorption is important chiefly because it is one of the essential steps in catalytic reactions (see *Catalysis*). It is generally believed that at least one of the reactants of a catalytic reaction has to be chemically adsorbed during reaction. A second application of chemical adsorption is its use in obtaining estimates of the fraction of the surface of certain metallic catalysts composed of metal atoms. Thus, for example, iron-synthetic ammonia catalysts containing a few per cent of aluminum oxide and potassium oxide as promoters appear to have about one third of their surface covered with iron atoms and the other two thirds with the promoter molecules. This can be established by comparing the chemisorption of carbon monoxide with the volume of nitrogen required according to the BET theory to cover the entire surface of the catalyst.

Until recently no means existed for telling in detail the properties of molecules chemisorbed on the surface of a catalyst. Recently an important step has been taken toward obtaining more detailed information about the exact nature of the binding of molecules on solid surfaces. Eischens, Pliskin and Francis have succeeded in obtaining the infrared absorption spectra of carbon monoxide chemisorbed on the surface of metals such as Fe, Ni, Co, Pt, Pd, and Cu. The tiny metal crystals, in turn, are supported on finely divided silica. The absorption spectra of the adsorbed molecules seem to differ from the spectrum of gaseous carbon monoxide in all instances; there is at least a suggestion that the spectra are especially different for those catalysts that are most effective in catalyzing reactions involving carbon monoxide.

Adsorption from the Liquid Phase. Adsorption in the liquid phase is perhaps even more important than adsorption of gases on solids. It apparently is an essential feature of many colloidal processes that play a part in plant and animal growth. However, the systems gas-liquid, liquid-liquid, and liquid-solid which comprise this type of adsorption are much less well understood than the simpler gas-solid adsorption. Accordingly, only a few generalities in regard to such systems will be covered.

Systems in which a single liquid phase exists

may involve adsorption either of gases or of a dissolved substance on the surface of a liquid. Relatively little is known about the first of these two because of the experimental difficulties encountered. Mercury appears to cover itself with gases or vapors at room temperature to form approximately a monolayer. The surface tension of the mercury is lowered somewhat in the process, the extent of lowering being probably in the range 5 to 10%.

Solutes frequently tend to concentrate in the surface of a solvent in which they are dissolved. Those which are thus adsorbed at the surface are said to be "surface-active." As a rule such materials lower the surface tension of the liquid in the process of being adsorbed at the surface. The well known Gibbs' equation is an expression of the relation between the change in the surface tension, σ , and the excess number of solute molecules present in each square centimeter of the surface, Γ . The equation may be written in the form

$$\Gamma = -\frac{c}{RT} \frac{d\sigma}{dc}$$

where c is the concentration of the solute in the bulk of the liquid, R is the gas constant, and T is the temperature. As is evident, the concentration in the surface will be greater than that in bulk only if $d\sigma/dc$ is negative; the excess will be negative (corresponding to the dissolved molecules tending to concentrate in the bulk of the liquid with the formation of a surface composed largely of solvent molecules) if the change in surface tension with concentration is positive. Much experimental work has been done in an effort to confirm the Gibbs' equation experimentally. Many of the data conform well to the equation. Other data do not seem to follow it too well. For the most part, however, it is recognized as one of the basic adsorption equations in liquid-gas and liquid-liquid systems.

Liquid-liquid systems resemble pure liquid systems in respect to adsorption of dissolved substances at the interface. The general rule in this case is that substances tending to lower the interfacial tension between two liquids will be adsorbed at the interface, whereas substances which raise the interfacial tension will stay dissolved in the liquid phase and will not concentrate at the interface.

Liquid-solid systems are of special interest though they are less well understood than liquid-gas systems. Perhaps the most important characteristic of the adsorption of solutes from liquids onto solids is the fact that such adsorption is necessarily highly competitive between the molecules of the solvent and those of the solute, and it will therefore depend upon the properties of the solute, the solvent and the adsorbent.

Two special applications of adsorption from the liquid phase should be mentioned because of their utility in modern chemical technology. These are chromatography and ion exchange.

Chromatography involves the preferential adsorption of components from a solution during passage of the latter through a column of finely divided solid. Each separate component because

of its own unique adsorptive properties collects in the column as a band. These bands can be removed in various ways with the recovery of the pure adsorbate. Commonly the various bands are eluted from columns by passage of a solvent that is more strongly adsorbed than the dissolved components. This valuable application which has now become a standard tool in organic chemistry is but another illustration of the importance of adsorption from solutions (See *Chromatography*).

Ion exchange is a special phenomenon sometimes included in the general meaning of the word adsorption. When ionic solutions are passed over certain types of adsorbents, the cations or anions from the solutions can be made to exchange with the cations or anions on the adsorbent. Thus the process can be made to remove a particular ion from solutions in much the fashion in which dissolved components are removed in chromatography. This procedure is commonly used in water softening. Zeolites or resinous ion exchangers can be prepared that will, for example, remove calcium ions from a solution and replace them with sodium ions, hydrogen ions or some other harmless ion from the solid ion exchange agent. The procedure is really a surface-chemical reaction, since it does not involve the simultaneous removal of both the cations and anions from solution but only a replacement, in this example, of one cation by another. (See *Ion Exchange*).

PAUL H. EMMETT

Cross-references: *Catalysis, Absorbents, Surface Tants, Chromatography, Carbon (Activated), BET Theory*

AEROSOLS

Aerosols are particles of solid or liquid suspended in a gas phase. Water fogs, salts from evaporation of ocean spray, and volcanic ash are examples of aerosol systems of natural origin; those of man-made origin are innumerable. Their properties are of interest where it is desired (1) to produce and stabilize them for technological reasons, (2) to suppress their formation or, (3) to destroy them by separating the particle from the gas phase.

Aerosols may be produced by simple mechanical dispersion of powdered materials, by condensation of vapors in cooling below the dew point (liquids) or the snow point (solids), by combustion processes (e.g., smoke), or by atomization of liquid suspensions of solids or of liquid solutions followed by evaporation. The last process is exemplified by various commercial products for domestic consumption, e.g., insecticides, a development, incidentally, that has popularized the term "aerosol" and sometimes distorted its scientific meaning.

The method of formation markedly affects the degree of dispersion of the resulting aerosol. Mechanical dispersion of powder in a blast of high velocity air is sometimes quite ineffective in completely breaking up aggregates into their entities. The efficiency of methods involving atomization of liquids is dependent on the concentration of

solids in the liquid and on the size of the droplet resulting from atomization, since these factors determine the chances of any droplet which is to evaporate containing more than one particle. The atomization of liquids in a high velocity air stream results in droplets whose minimum average diameter is given by $d_m = \frac{585}{V} \sqrt{\frac{\sigma}{\rho}}$ where d_m is diameter in microns, σ is liquid surface tension in dynes per cm. and ρ its specific gravity. The extent to which this size is exceeded is dependent on the relative quantity flow of liquid and air as well as on the physical properties of the liquid.

Aerosols of uniform particle size can be formed by volatilization of a suitable liquid and subsequent condensation but care must be accorded to such critical factors as vaporization rate, temperature, gas flow rate, formation and introduction of condensation nuclei.

Aerosols are inherently unstable in contrast to hydrosols, the degree of stability being determined principally by the concentration and particle size characteristics. Concentration is important as it determines the rate of coagulation. For the special case where all particles are of nearly uniform size,

the resulting decay rate $\frac{dN}{dt} \propto N^2$, where N is number concentration and t is time. The rate is independent of particle size except for smaller particles which approach the dimensions of the mean free path (approximately 0.1 micron at normal temperature and pressure). At a concentration of 10^5 particles of uniform size per cubic centimeter about one-tenth of the particles would coagulate in one hour.

Sedimentation of spherical particles by gravity occurs at velocities determined by Stokes' Law, which is applicable without excessive error also to most irregularly shaped particles. At ordinary air temperature and pressure the terminal settling velocity is given by $u_t = 3 \times 10^{-4} Z d_m^2$, where u_t is velocity in cm. per sec., Z is specific gravity and d_m is particle diameter in microns. This expression is limited in application to particles smaller than 50-100 microns; and below about 1 micron the value is increased somewhat due to the Cunningham mean free path correction.

Aerosol systems are also subject to other destructive forces: convection, Brownian diffusion, thermal repulsion and photophoresis. Convection currents transport portions of the gas continuously to points adjacent to solid surfaces, such as container walls, where Brownian motion operates to drive particles through the adjacent gas layer for deposition on such surfaces. Particles suspended in gas which is at a higher temperature than a nearby surface will migrate toward the cold surface at a rate which is proportional to $\frac{dT}{dx}$, where T is temperature and x is distance.

Motion of small particles is also induced by the little understood process of photophoresis, wherein the particles migrate along the axis of an intense light beam, usually away from the source.

No surface protective agents are known, analogous to the protective colloids of hydrosols, which will stabilize hydrosols against these various processes. Stability is enhanced only by small particle size, a high degree of dilution, minimum enclosure surface per unit volume and uniform temperature conditions.

Varying degrees of electric charge are acquired by aerosol particles in various circumstances, but it is not believed that they have any important influence on coagulation of particles. This phenomenon, however, has not been studied thoroughly. Interaction between charged particles and nearby surfaces does occur, however, at measurable rates, but the knowledge on this phenomenon is limited and rests on an empirical base.

Separation of the particles from the gas can be effected with varying degrees of efficiency and energy requirement by exploiting inertial characteristics (as in centrifugal devices and coarse filters for removal of particles larger than 5-10 microns), by electrical precipitation, by the diffusion due to Brownian motion (applicable to filtration of particles smaller than about $\frac{1}{4}$ micron), by electrostatically charged filters, by arrangements causing thermal precipitation, as well as by some coagulation in conjunction with one of the inertial processes. All of these have been applied both to large scale air and gas cleaning and to instruments for measurement of concentration except thermal precipitation which has been confined to instrumental applications.

Measurement of the weight concentration of the typical aerosol of heterogeneous size distribution inevitably emphasizes the concentration of the largest particles of the size spectrum, indicating little or nothing of the quantity of the smallest particles present in the mixture. For this reason care should be exercised to insure that a weight determination is properly suited to the purposes of the measurement. Such a determination can be made by operation of gas sampling apparatus which effects a separation of the aerosol particles from the gas phase by filtration or by electrical precipitation, both providing high efficiency. Separation by high velocity impingement of the gas stream onto an adhesive-coated plate (impaction), by centrifugal separation apparatus or by liquid hoppers is generally limited to particles larger than about 5 microns unless the apparatus is of special design.

Size characteristics of aerosols of uniform particle size can be determined effectively by measurement of their light-scattering properties, law of which have been well developed. The more usual aerosol of heterogeneous size properties can be effectively studied optically only by empirical methods involving measurement of light scattering. Various systems are available for the purpose, ranging from low sensitivity arrangements which merely indicate reduction in quantity of direct light transmission, to highly sensitive photomultiplier systems which measure forward or lateral scattering and are sensitive enough to measure difference in light scattering of gas molecules.

Aerosol particles range over a broad band of sizes with indefinite limits. Technological interest has been largely confined to those within the range 0.1 to 100 microns diameter, depending on the nature and time scale of the phenomenon. Concern with optical phenomena is pretty much limited to those particles whose diameter is less than about 10 microns; inertia and sedimentation are of primary interest in application to particles larger than 5 or 10 microns and consideration of coagulation applies principally to particles below 1 micron mainly because gravity sedimentation greatly predominates for larger particles.

W. C. L. HEMMON

Cross-references: Air Pollution, Colloid Chemistry, Pesticides, Sol, Precipitation (Stokes Law), Brownian Motion.

AGRICULTURAL CHEMISTRY

In the latter part of the 19th century and the first part of the 20th, the term "mechanization of agriculture" was heard throughout the country. It made possible the feeding of a very rapidly expanding population. It provided this greatly expanded population with more crops, better nutritional values, improved health, greater life expectancy, etc. In more recent years a new term has come into rather widespread use: "chemicalization of agriculture". Again the net result has been the same—still greater quantities of food, feed, and fibers for an increasing population and a rapidly expanding industrial economy.

What is agricultural chemistry? Donald E. H. Frear, editor of the two-volume treatise "Agricultural Chemistry" in the preface to Volume I, defines it in its broadest sense as a field that embraces every phase of chemistry as it is related to the growing and processing of economic plants and animals. The field of agricultural chemistry is one that continues to broaden at an almost unbelievable pace. This has been particularly true of the past couple of decades, in which many brilliant minds have researched in the fields of fertilizers, pesticides, plant regulators, etc.

The history of the use of natural manures to improve soil conditions is lost in antiquity. In the Western Hemisphere early settlers found the Indians following the practice of placing a fish head near each stalk of corn. Obviously our ancestors employed decaying organic matter as a fertilizer to stimulate plant growth but did not understand the scientific principles involved. Nevertheless, this crude understanding of what happened when organic matter was added to the soil in helping to grow more and better food, feed and fiber, was the beginning of the "chemicalization of agriculture".

Four momentous discoveries of latent natural resources made possible what, for the lack of a better term, must be called "commercial fertilizer". One such discovery was the finding of the rather limited guano deposits on a barren island off the west coast of South America. Still another was the uncovering of the vast Chilean nitrate deposits; a third, the more or less accidental discovery of potash salts in large quantities in cer-

tain parts of Western Europe. In this series also was the discovery of large phosphate deposits in many parts of the world, including Florida, North Africa, on one or two island in the Pacific, in the State of Tennessee, and in more recent years in one or two of the western states.

Thus at long last chemists had at their command reasonably adequate supplies of the three basic essentials of a fertilizer: nitrogen, potash, and phosphate. These four discoveries did much to overcome the belief of many in the Malthusian theory, to the effect that the population of the world would quickly outstrip the world's ability to grow sufficient food to prevent wholesale starvation.

The story of the fixation of nitrogen from the air has been told many times, and need not be repeated here. Sufficient to say that the world's complete dependence on natural organic materials and guano and Chilean nitrates ceased to exist after the great German chemist and chemical engineer Haber demonstrated that by use of chemical technology nitrogen could be "harnessed" and made available for agricultural purposes in unlimited quantities. The Haber process is not the only method employed for the fixation of nitrogen, but in modified forms it is today the most widely used method employed throughout the world. The so-called "cyanamid" process is used rather extensively in some parts of the world, a process actually developed prior to the perfecting of the Haber process.

The volume of food, feed and fiber produced depends not only on the soil conditions under which these crops are grown, but likewise is dependent upon the success that man has in thwarting ravages caused by innumerable pests and fungi. The volume also is related to man's success in destroying rodents and other pests that eat or destroy crops after being harvested.

For many years pesticides and fungicides were limited almost exclusively to inorganic compounds, such as the various arsenates, copper sulfate, Paris green, etc. Perhaps the most widely used organic pesticide in the past was nicotine sulfate. In more recent years a whole flood of new organic pesticides, fungicides, etc., have been developed, with new ones being added with almost bewildering rapidity; these have completely revolutionized the farmer's ability to cope with the ravages and plant diseases caused by insects or fungi.

Today the term "agricultural chemistry" encompasses a very wide variety of interests in the use of fertilizers, pesticides, plant regulators, etc. Chemists, biochemists, agronomists, soil scientists, entomologists, physicists, and a host of other professions are exploring the very basic concept of plant growth. This is equally true in the area of animal chemistry. It is a reasonable expectation that from this research will come tremendous changes. The result of "chemicalization of agriculture" will be much more profound and far-reach-

ing than those caused by the "mechanization of agriculture".

Certainly one very direct result that we are seeing is the trend towards larger and larger farming units. More and more agriculture is becoming a specialized form of industry rather than a traditional way of life. Both the "mechanization of agriculture" and the "chemicalization of agriculture" tend to bring about more scientific approach to the growing of food, feed, fiber and animals. This materially leads to "centralization" of these efforts.

WALTER J. MURPHY

Cross-references: *Pesticides, Haber, Chemurgy*

AGRICULTURAL RESEARCH INSTITUTE

The Agricultural Board was conceived to embody scientific leadership in agricultural policies and practices. The Agricultural Research Institute was conceived as an organization to support the Agricultural Board financially and to provide the mechanism for exchange of information and viewpoint between industrial and agricultural scientists.

Members and officers of the Agricultural Board are appointed by the National Research Council. Membership of the Agricultural Research Institute is composed of organizations who have applied and been accepted for membership and who designate individuals to represent them. Officers of the Institute are elected by the representatives of member organizations as specified in the by-laws. Neither controls the other, but lines of communication are open through a joint secretarial staff employed by the National Research Council.

(1) It enlists the scientific talent of governments, industry, and the universities for membership on committees competent to comprehend the broad problems of agriculture and determine the order of priority for attacking them. (2) It collects facts and evaluates existing knowledge in relation to probable results of present policies or practices in agriculture. (3) It objectively surveys and correlates trends in present research in relation to neglected areas most likely to yield profitable longtime results. (4) It disseminates knowledge and expedites the transition of research discovery to applications in agricultural and industrial operations, governmental policies, or socio-economic affairs of a population increasingly dependent on technology.

(1) It provides funds for the effective functioning of the Agricultural Board. (2) It keeps the Agricultural Board alert to the multitude of forces that determine the course of industrial development in fields which are directly or indirectly related to agriculture, provides information, and suggests pertinent problems for review. (3) It disseminates among its members the judgments and resultant implications and applications of the Board's activities.

AIR

The atmosphere, or air, is the gaseous envelope that surrounds the earth and even penetrates into it to some extent. Air is a mixture because: (1) The composition of air varies slightly, more than can be accounted for by experimental error; the composition of a compound, on the other hand, is constant. (2) Air has the boiling points of its several components, and not one single boiling point at a given pressure. Compounds have one single boiling point. (3) When air containing 21 per cent oxygen by volume is dissolved in water, and the air is later removed from the water, the percentage of oxygen recovered in the resulting gas is 35 per cent. If air were a compound there would be no change in composition upon dissolving and recovering. (4) When air diffuses through a porous membrane or piece of porous porcelain, the lighter nitrogen molecules pass through more readily than the heavier oxygen molecules. The resulting air changes in composition. A compound shows no change in composition after such a diffusion. These facts are all evidence that air is a mixture and not a compound.

Analysis of air is usually made after it is freed from solids such as dust, spores, and bacteria, and water vapor. The following is a representative composite of anal. of dry air

Substance	% by Weight	% by Volume
Nitrogen, N_2	75.53	78.00
Oxygen, O_2	23.16	20.95
Argon, A	1.27	0.93
Carbon dioxide, CO_2	0.033	0.03
Neon, Ne		0.0018
Helium, He		0.0005
Methane, CH_4		0.0002
Krypton, Kr		0.0001
Nitrous oxide, N_2O		0.000,05
Hydrogen, H_2		0.000,05
Xenon, Xe		0.000,008
Ozone, O_3		0.000,001

The composition of air varies with altitude at which the sample is taken. Most of the shorter waves of radiant energy that reach the earth from the sun are absorbed in the stratosphere, about 15 miles above the earth. The reaction $3O_2 \rightarrow 2O_3$ is caused by these waves in the ultraviolet region of the spectrum, producing an ozone-rich region of the atmosphere.

The air, of course, is the source of oxygen for burning, respiration of plants and animals, decay, and industrial oxidations. Some of these processes return CO_2 to the air, in which it is present in the amount of 0.03% by volume. Thus the air is the source of the CO_2 utilized in the weathering of rocks and in photosynthesis (carbon cycle). Photosynthesis returns oxygen to the air. The changes such as those mentioned more or less offset one another, and the winds keep the air well mixed. Variations in composition are usually caused by some local effect.

Liquid air is the source of oxygen that is used extensively, and marketed in steel tanks under high pressure. When liquid air boils, nitrogen distills first at $-196^\circ C$, and then oxygen at its boiling

point, $-183^\circ C$. When liquid air is fractionated at $-196^\circ C$ to prepare nitrogen, the resulting gas contains about 1.25 per cent inert gases. This mixture is used to fill electric light bulbs, to pack with oxidizable foods such as ground coffee in cans, and to maintain pressure in excess of atmospheric within telephone cables.

The inert gases, except helium, are obtained from air. The fraction from liquid air that contains the inert gases consists of 60 per cent argon, 30 per cent oxygen, and 10 per cent nitrogen. Hydrogen is added to combine with oxygen and remove it as water vapor, which can be readily separated. The commercial mixture that remains is used to fill electric light bulbs. It contains 85 per cent inert gases, chiefly argon, and the balance nitrogen.

Isolation of neon, krypton, and xenon from the air is a difficult process. Fractional distillation first makes a gross separation. Oxygen in the mixture can be removed by combining it with hydrogen or by passing the gas over hot metallic copper with which the oxygen forms copper oxide. Nitrogen is then removed by passing the gaseous mixture over hot magnesium. The nitrogen combines with this metal and forms magnesium nitride (Mg_3N_2). Adsorption of the remaining inert gases by activated charcoal is at different rates, as is desorption. If charcoal at a low temperature is saturated with a mixture of inert gases, and then the temperature raised to $-80^\circ C$, the gas that escapes is almost pure argon. Chemical means are used to purify the inert gases, but physical means must be used to separate them.

For a more detailed description of the air, the reader is referred to works on Meteorology, a study that includes the circulation of the air, clouds, effects of altitude and pressure, and the prediction of weather.

ELBERT C. WEAVER

Cross-references: Nitrogen, Oxygen, Neon, Gas Laws, A Pollution

AIR POLLUTION

Pollution of the atmosphere may be objectionable because of (a) its health aspects, (b) deleterious effects on vegetation or animals, (c) corrosion of materials, or (d) its nuisance effects. With the exception of a few isolated cases there is no concrete evidence establishing the relationship between common types of air pollution and chronic health effects, although there has been considerable speculation concerning a relationship between lung cancer and fuel smoke. In the case of acute health effects the evidence is clear-cut as in the case of an episode in the Meuse Valley (1930), several in England and the Donora smog (1948). In all these instances effects were evidently related to the ability of the pollutant to cause irritation of the respiratory tract, but the specific irritant in the atmosphere was not identified.

Many of the toxic dusts and gases that are of concern in industrial health protection are found in the outdoor atmosphere but in concentrations that are but a small fraction of those that engage

the attention of workers in industrial hygiene. Typical concentrations in United States cities: total solids 100-500; lead 0.5-5; manganese 0.1-0.5; cadmium 0.01-0.1; (units in micrograms per cubic meter). Concentrations regarded as acceptable in in-plant exposures are as follows: lead 150, manganese over 6000, and cadmium (fume) 100. On the basis of present knowledge, therefore, there does not appear to be any reason to suppose that systemic toxic effects occur, as distinguished from any that may result from deposition of an irritant substance in the respiratory tract.

Damage to vegetation results from exposure to low concentrations of a number of gases, but those of primary economic significance are sulfur dioxide and hydrofluoric acid. Significant concentrations are dependent on many factors, e.g., type of plant and its age, season, humidity, light conditions, time of exposure and character of soil. In the case of sulfur dioxide in favorable conditions one-half part per million may produce significant effects in some plants. In the case of hydrofluoric acid gas concentrations one tenth of those or even less may produce deleterious results in sensitive plants.

Aside from its effects on vegetation, sulfur dioxide occupies a prominent place in atmospheric pollution because of its widespread occurrence due to the combustion of sulfur-containing fuels. One of its properties of economic concern is its well-known ability to aggravate the corrosion of materials. It is also suspected of contributing to an irritant quality of the atmosphere in acute smog episodes. The spontaneous oxidation of sulfur dioxide gas is assisted by actinic energy in sunlight, high humidity and by the catalytic effect of particulate matter in atmospheric suspension.

Nuisances such as those due to deposited dirt, decreased visibility and foreign odors are of *subjective* nature and it is therefore inherently impossible to fix limits of concentrations or intensity to define such conditions, in contrast to the *objective* effects cited above. In the interpretation of the measurements of air pollution nuisances, therefore, one must resort to the adduction of comparative data. The most common and widespread atmospheric problem stems from the burning of coal, both in domestic and industrial equipment, giving rise to two distinct types of air pollution: that due to smoke which is avoided by efficient combustion of volatile material of the fuel and that due to fuel dust which is blown off the fuel bed or, in industrial installations, to the incombustible ash fraction from the burning of pulverized coal. Standards of good practice for the control of solids emissions from coal-burning installations having common acceptance are based on (a) the use of the Ringelmann chart for describing limits on smoke emission and (b) on the determination of weight concentration of solids in the flue gas.

Methods that are appropriate for measurement and analysis of air pollution intensity at ground level are dependent on the objective. If the purpose is to ascertain the origin of the pollution, the entire gamut of scientific techniques may be applied, as in the Los Angeles problem (1945 et.

seq.). If the objective is simply to establish levels of atmospheric pollution for historical purposes, i.e., time comparisons, or for geographical comparisons, a relatively few techniques suffice.

Where, for example, it is sought to establish records of the coarse dust content in the air which deposits by gravity, dust fall observations can be made by determining the rate at which solids are deposited within an open top vessel. When a cylindrical vessel with a continuously wet bottom is employed (U. S. practice) and the results expressed in the units, tons per square mile per month, the following figures may be taken as typical of those in the northern United States: suburban areas (summertime) 5-15, (wintertime) 10-20; in urban residential areas removed from nearby industrial sources (summertime) 10-30, (wintertime) 20-60. Analogous measurements for smoke content of the atmosphere have a relatively brief history and procedures are less standardized. One common method used in Great Britain and the United States involves measurement of the light scattering or staining potential of smoke that has been deposited by aspiration onto a filter paper. Similar data can be obtained by direct measurement of light scattering in suitable electrophotometric devices.

In the case of odors there is no objective basis for measurement, except in a few instances where the odor chemistry is well known and it becomes necessary therefore to rely entirely on subjective impressions of humans. This circumstance proposes nearly insuperable problems in the evaluation of odor intensity in the open, but odor measurements in a stream of gas at the point of emission are readily employed in objective analyses. Such measurements are effected by instrumental arrangements in which the odor-carrying gas stream is diluted in known proportions with fresh air, and the dilution ratio value corresponding to zero odor threshold determined subjectively by a number of persons. The result can be related to estimates of dilution occurring by natural turbulence between the point of emission and some point at ground level or to the performance of a pilot odor removal unit.

The concentration of air pollution in any locality is profoundly influenced by the natural rate of ventilation characteristic of the place and the time, as well as by the rate at which pollutants are emitted to the atmosphere. Ventilation results not only from horizontal winds, but also from vertical air currents, which are largely determined by the relative temperatures of the atmosphere at different elevations. When, due to such temperature variation, the air layers nearer the ground level are more dense than those aloft, vertical motion of the atmosphere and consequent dispersal of polluted air is prevented. This condition termed *inversion* by meteorologists occurs almost every night and not infrequently is persistent over a longer period of time. Due to meteorological and geographical peculiarities some regions are characteristically ventilated at greater rates than others. This meteorological circumstance is largely responsible for the commonly observed wide varia-

tions in air pollution intensity in consecutive periods.

The concentration of any pollutant at ground level due to emission from a single source is directly proportional to the mass rate of emission, to the wind velocity and to the square of the chimney height, as well as to a variable parameter incorporating meteorological factors that describe the prevailing atmospheric turbulence. The location of the point of maximum ground level concentration varies markedly with the meteorological conditions but falls most commonly at a distance of 5 to 25 stack lengths from the source. A theoretically derived expression for certain common meteorological conditions gives this maximum concentration (mass per unit

volume) as $\frac{2Q}{\pi u h^2}$, where Q is rate of emission of the contaminant, (mass per unit time), u is wind velocity and h is stack height, employing consistent units. Corresponding equations for concentrations at variable distance are complex because they are dependent upon atmospheric conditions of turbulence which are not readily defined in quantitative terms.

The abatement of air pollution when the sources are identified is almost entirely an economic problem. Coal smoke is only controllable practically by automatic arrangements for efficient combustion. This has not been found applicable to the domestic coal smoke problem; substitute fuels have reduced that problem in many areas. Dust emissions can be suppressed by application of various types of collectors listed, as follows, in the order of their characteristic collection efficiency: bag filters, Cottrell precipitators, and the miscellaneous group that includes centrifugal precipitators, inertial separators and water scrubbers. Technologically, sulfur dioxide can be removed by conventional scrubbing techniques, but insuperable economic problems have appeared in considering its applicability to large fuel burning installations.

Odorous elements of organic nature can be destroyed by heating the gas stream to a temperature of approximately 1500°F and, in the presence of a catalyst, to about 500°F excepting in some particular circumstances. If the odorous substance is present in very small quantities, it is sometimes feasible to absorb it in activated carbon.

Dilution of moderate quantities of gases can often be effected by the use of tall stacks, a method that is commonly applied to the sulfur dioxide problem. It is to be noted that initial dilution in the stack itself is without effect.

W. C. L. HEMMON

Cross-references: *Acrosols, Air, Precipitation*

ALBUMIN

The word "albumin" is derived from the Latin "album" (white). It is one of the classes of simple proteins, defined as being soluble in pure water and coagulated by heat. The name was derived from albumen, egg white, since the principal protein of egg white is the classical example of an

albumin. Albumins are found in various plant and animal tissues, and are generally named according to their source, e.g., egg albumin or ovalbumin from eggs, serum albumin from blood serum, myoalbumin from muscle, etc.

The definition of albumin is actually inadequate for at least two reasons. In the first place, albumins are defined as being simple proteins, containing no constituents other than amino acids. It is now recognized that simple proteins, in the strictest sense, are relatively rare. Even the classical example, hen's egg albumin, contains a small amount of carbohydrate and phosphoric ester groups. In practice, then, this part of the definition has actually been abandoned unless the non-amino acid portion exceeds several per cent.

The second difficulty with the official definition is that it does not take account of the effects of pH upon the solubility, since these effects had not been adequately described in 1907. Most contemporary protein chemists would probably be inclined to define albumins as being "soluble in the absence of salt at the isoelectric point and coagulated by heat".

A third difficulty with the definition of the term albumin is due to the protein chemists rather than to the official definition. It has been customary to precipitate the globulins from a mixture of soluble proteins with half-saturated ammonium sulfate or a comparable concentration of sodium sulfate or other salting out agent. As early as 1912, in his book "The Vegetable Proteins", Thomas Osborne pointed out the fact that many plant proteins which were precipitated with half-saturated ammonium sulfate behaved as albumins with respect to their solubility in distilled water. Howe later recognized the same problem with respect to the blood serum proteins, and introduced the term "pseudoglobulin" to designate such proteins. Thus, some of the serum proteins which are now commonly grouped with the globulins should properly be called albumins according to the official classification.

Ovalbumin. Different albumins are present in the eggs of various species, but most attention has been devoted to that from the hen's egg. Ovalbumin makes up about 65% of the total protein of egg white. It appears to be quite homogeneous, except for the number of phosphoric acid ester groups. Most of the molecules have two, a smaller number one, and a trace none. Carbohydrate appears to be an integral part of the molecule, there being 1.7 to 1.8% hexose, probably mannose, and 1 to 1.4% hexosamine. Since there is evidence for a terminal carboxyl group (alanine) in the polypeptide chain, but none for a free terminal amino group, the carbohydrate may be attached to the terminal amino group.

Conalbumin. A second albumin has been crystallized from egg white. This protein, making up about 14% of the protein of hen's egg white, has been recognized since 1900. It may be prepared in a form which is apparently free from any groups except amino acids, but combines strongly with two ferric ions and two bicarbonate ions per mole. In the absence of iron, cupric or zinc ions may be

bound at the same site. The groups involved in the binding are not known, but there is some suggestion that phenolic groups may be involved. If so, they must be in a very specific environment, since there are 19 or 20 tyrosine residues per mole.

Serum Albumin. All of the blood sera or plasmas of the vertebrates which have been studied contain a large proportion of an albumin fraction which is relatively homogeneous by most criteria. This fraction, amounting to about 50% of the total protein, remains in solution in half-saturated ammonium sulfate at pH 7 (about where the salt fractionation is usually carried out), migrates as a single peak in electrophoresis at a pH above 5, and seems to have a single sedimentation constant for a given species. This is what is ordinarily referred to as serum albumin. Crystallization of horse serum albumin can readily be effected by an ammonium sulfate procedure, and this was originally the serum protein most thoroughly studied. During World War II, it was desired to prepare large amounts of human serum albumin to restore plasma volume in the treatment of shock. A fractionation procedure employing alcohol at low temperatures was developed by Cohn and co-workers, and as a consequence human serum albumin has become commercially available. Since the use of animal albumins for administration to man was also being considered, the preparation of bovine albumin was also carried out commercially by Armour and Co.

However, it has been clear for some time that such preparations are mixtures of closely related molecules. For example, one part of horse serum albumin can be crystallized from concentrated, salt-free solutions, and is found to contain no carbohydrate. Other crystalline fractions of horse serum albumin do contain carbohydrate. Although showing only one electrophoretic peak above the isoelectric point, the albumins of the horse, cow, man, and rat have at least two electrophoretic peaks below the isoelectric point. About two thirds of the human serum albumin has one reactive sulfhydryl group per mole, and the remainder has none. In the case of rat serum albumin, about two thirds of the total has a much greater affinity for one mole of zinc than the balance. These albumins can, then, be further fractionated on the basis of the specific behavior with mercury or with zinc. It should be quite clear from these comments that the pure or crystalline serum albumins that have provided the physical and chemical data in the tables are really mixtures, and we can not be sure how great the differences are between the components of the mixtures.

One rather striking property of the serum albumins is their tendency to bind negative ions, even in the face of a negative charge on the protein. This property is not restricted to the albumins, but is most markedly shown by them, and may represent one of the important physiological properties of the serum albumins. The binding of organic ions generally increases with the size of the non-polar portion of the molecule, and highly purified preparation of serum albumins have generally been found to contain small amounts of higher fatty acids. Indeed, such traces of fatty acid in-

crease the stability and ease of crystallization of the protein.

JOHN MEHL

Cross-references: *Amino Acids, Proteins, Blood*

ALCHEMY

Alchemy is usually defined as the art whose principal objectives were (1) the transmutation of base metals to gold and silver and (2) the discovery of the panacea or universal remedy. However, in a larger sense, from the time of its origin in China (ca. 600 B.C.) to the sixteenth century, alchemy was the chief repository of the theoretical and factual knowledge of chemistry. Chemistry did not break abruptly from alchemy but grew out of it.

Alchemical theory was based on the hypothesis that all matter was composed of one primal material. The various elemental forms that this material might take, e.g. "air", "earth", "fire" and "water", were believed to result from the combination of its active and passive or male and female principles, these gave rise to the fundamental opposing qualities: hot and cold, wet and dry. On this basis, it could be assumed that the existence of any given form of matter depended upon a specific balance of opposing principles. Therefore, it followed that one form could be converted to another by modification of this balance. It should be noted that this hypothesis is not in harmonious with modern theories concerning protons and electrons in the elemental atom. Alchemists believed that an understanding of the constitution of matter would accordingly make it possible to change base metals to gold. Gold was recognized as the purest representative of the metallic essence because of its luster and its resistance to corrosion and the effects of age. It was also believed that knowledge of the factors which gave gold its permanence would lead to a solution of the problem of human longevity.

Alchemy is often discredited because of the quacks and charlatans who practiced it. Since the lives and deeds of these persons are more colorful and easier to understand than the philosophy of the serious scientist, alchemy is usually regarded as a "racket" rather than a science. It must be remembered that transmutation remained a legitimate research objective until its impossibility with the equipment at hand had been adequately demonstrated. This required the development of an understanding of chemical purity, chemical elements and chemical compounds. Alchemical investigation laid the groundwork for the solution of these problems.

Chemistry was born when alchemists gave up the attempt to fathom the constitution of matter and confined their investigation to the more tangible chemical elements. In the years that followed, speculation on the composition of the elements was frankly taboo. As a result, Prout's hypothesis and early indications of the periodicity of elemental properties were not readily accepted by later chemists. However, the alchemical hypothesis was finally corroborated by the discov-

eries of nuclear science. Unlimited energy has now replaced the golden dream of transmutation.

J. FREDERIC WALKER

Cross-references: *Chemistry (History)*

ALCOHOLS

Chemical Aspects

The word "alcohol" is derived from an Arabic term meaning a powder for painting the eyelids; it was later applied to highly rectified spirits. Alcohols are hydroxyl derivatives of hydrocarbons. There may be one or several hydroxyl OH-groups in the molecule; however, only one such group may be attached to a single carbon atom.

Class	Example
I. Simple aliphatic alcohol	Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$)
II. Unsaturated aliphatic alcohol	Allyl alcohol ($\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$)
III. Substituted aliphatic alcohol	Ethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$)
IV. Aromatic alcohol	Benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$)
V. Alicyclic alcohol	Cyclohexanol ($\text{C}_6\text{H}_{11}\text{OH}$)
VI. Heterocyclic alcohol	Furfuryl alcohol ($\text{C}_4\text{H}_3\text{OCH}_2\text{OH}$)

Alcohols are further classified as monohydric, dihydric, trihydric, etc., according to the number of hydroxyl groups they contain. Ethylene glycol is an example of a dihydric alcohol. $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$, glycerol is trihydric, sorbitol is hexahydric, etc. Alcohols are also classified by the number of hydrogen atoms attached to the carbon atom holding the hydroxyl group. If two or more hydrogen atoms are attached to the carbon holding the hydroxyl, the alcohol is primary; if only one, the alcohol is secondary; and if no hydrogen is attached, the alcohol is tertiary.

Properties. Alcohols in general are colorless liquids or solids. The simpler monohydric alcohols are mobile liquids, and viscosity increases with molecular weight. N dodecyl alcohol is the first solid member of the series of normal primary alcohols. Polyhydric alcohols are syrupy liquids. Alcohols with more complex formulas are generally solids. In general, water solubility decreases as the formula becomes more complex. Boiling points increase as the straight-chain alcohols become more complex. Unless influenced by other groups, the reaction of alcohols are primarily those of the hydroxyl group. This group may be replaced by halogen or amino groups. The alcohol may be dehydrated or the hydrogen of the hydroxyl group replaced by a metal. Alcohol will form esters with an organic acid by the elimination of water.

Methyl alcohol (methanol, wood alcohol) is produced by destructive distillation of wood or by synthesis under pressure of hydrogen and carbon monoxide. Production amounted to 170,000,000 gallons for the fiscal year ended June 30, 1953. The pure product is completely miscible with water and is a solvent for fats, oils, resins and nitrocellulose. It is used widely for methylation of

organic compounds, particularly dyestuffs. It is the raw material for making formaldehyde and an intermediate in synthesis of phenolic, urea, and melamine resins. It is used in antifreeze solutions and in special fuels.

Ethyl alcohol (ethanol). The principal methods for producing ethyl alcohol are: (1) Fermentation of starch, sugar or waste sulfite liquor. (2) Synthesis from ethylene by hydration using sulfuric acid process. (3) Direct hydration of ethylene. (4) Synthesis from ethylene via ethyl chloride. (5) From acetylene by conversion to acetaldehyde and, hydrogenation to alcohol.

Both as anhydrous (200° Proof) and as 190° proof (95% by volume) it is sold as pure alcohol, or in a variety of formulas as completely denatured alcohol, specially denatured alcohol or proprietary solvent. It is used as a solvent or extractant in manufacture of lacquers, varnishes, stains, smokeless powder, cordite, antiseptics, toilet preparations, pharmaceuticals, and antifreeze solutions. Ethyl alcohol is also used as a building block in making many higher molecular weight chemicals. Total production of ethyl alcohol for industrial purposes amounted to about 270,000,000 wine gallons for the fiscal year ended June 30, 1953.

Isopropyl alcohol (isopropanol). This alcohol is produced by hydration of propylene from cracked gases and to a small extent as a by-product of certain types of fermentation in which normal butyl alcohol is the principal product. It is normally sold commercially as either 91% by volume (9% water) or 99% purity. It is soluble in water and is a solvent for many oils. It has many uses: as a coupling agent in the manufacture of soluble oils, as an extractant in purifying oils, and as a solvent for gums, alkaloids, oils, and resins. It is used extensively in chemical processes for making acetone and for introducing the isopropyl group. It is used in soaps and antiseptic solutions. It is also used for antifreeze. About 135 million gallons were produced during the fiscal year ended June 30, 1953.

Normal propyl alcohol is a co-product of air oxidation of propane and butane mixtures, as well as in the Fischer-Tropsch process. It is used as a solvent for lacquers and resin formulas. It finds use in brake fluids, and as a solvent in coatings, films and waxes. It is used in production of propionic acid and plasticizers. The quantity produced is not available in published statistics.

Butyl alcohol (n butanol) is produced either by fermentation of starch or sugar or by synthesis using ethyl alcohol or acetylene as raw materials. It is widely used as a solvent in nitrocellulose lacquers, for ethyl cellulose, urea-formaldehyde, and urea melamine resin formulations. It is a mutual solvent in soluble oils, a diluent in hydraulic fluids and an extractant in the manufacture of other pharmaceuticals. It is used in the chemical manufacturing field for making butyl xanthate, dibutyl phthalate and many other butyl compounds. The quantity produced was 24,000,000 gallons for fiscal year ended June 30, 1953.

Isobutyl alcohol is produced by synthesis from carbon monoxide and hydrogen at high pressure (300-700 atm.). The isobutyl alcohol is separated

by distillation from the mixture of *n*-propyl alcohol, active amyl alcohol, and other oxygenated products—it may also be made by hydrolysis of isobutyl chloride. Isobutyl alcohol can be used for esterifications of mono- and dibasic acids to form esters. It is used as a solvent for castor oil base brake fluids. It can also be substituted for normal butyl in the field of alkylated urea resins.

Secondary butyl alcohol is produced by hydration of 1-butane, which is formed in the cracking of petroleum. It can be used for making other chemicals such as methyl ethyl ketone by dehydration, acetate, xanthate derivatives. It is used as a latent solvent in nitrocellulose lacquers, in formulation of brake fluids, for industrial cleaning and as an extractant for fats and a solvent for special greases.

Tertiary butyl alcohol is produced by hydration of isobutylene derived from petroleum cracking. This alcohol is a white crystalline solid below 25.5°C. It is used for manufacture of tertiary butyl phenol or tertiary butyl chloride, in the perfume field for making artificial musk, and also as one of the components in wetting agents and detergents. The solvent uses are many in extraction of drugs and use in cleaning compounds. It also finds some use as a denaturant for ethyl alcohols. The production of all butyl alcohols except normal was about 35,000,000 gallons for the fiscal year ended June 30, 1953.

✓ *Amyl alcohols (pentyl alcohols)* occur in 8 isomeric forms, not including optical isomers. Isoamyl and active amyl alcohols, with minor quantities of some other alcohols, are separated by fractional distillation from fusel oil, which is a co-product in the production of ethyl alcohol by fermentation. They are also produced from a mixture of pentanes from natural gas. These alcohols are solvents for a large variety of natural and synthetic resinous materials. They are used as diluents in hydraulic fluids, also in printing inks and lacquers. A large part of the production (other than tertiary amyl) is made into amyl acetates and phthalates for use in lacquers and protective coatings. Amyl compounds are also useful in making medicinals and flotation products. Production of all amyl alcohols amounted to 20,777,000 pounds in the fiscal year ended June 30, 1953.

Higher saturated aliphatic alcohols. As the formulas become more complex, these alcohols range from oily liquids to viscous liquids and to wax-like solids. The number of isomers reaches astronomical figures. It is calculated to be 89 for octyl alcohol and 5,000,000 for a C₂₀ alcohol. Only a few are of commercial importance.

✓ *Ethylene glycol* is produced by (1) direct oxidation of ethylene to ethylene oxide and hydration to glycol; (2) ethylene to ethylene chlorhydrin, to ethylene oxide, to glycol; (3) hydrogenation of methyl glycolate made from formaldehyde and methanol. In these processes by-products such as propylene glycol, diethylene glycol, and triethylene glycol are produced. There are many uses for ethylene glycol such as antifreeze, hydraulic fluids, de-icing fluid, production of explosives, solvent for stains, oils, resins and enamels, in inks and dyes. The production of ethylene glycol was

67,000,000 gallons for the fiscal year ended June 30, 1953.

Diethylene glycol is produced mostly as a co-product in manufacture of ethylene glycol. Uses include hygroscopic agent, solvent for dyes and resins, anti-leak agent, gas drying, softening agent in adhesives, printing inks.

Triethylene glycol is produced as a co-product in manufacture of ethylene glycol. Uses include air disinfectant, production of resins and plasticizers, dehumidification.

Propylene glycol is made by the chlorhydrin process along with ethylene glycol or by direct oxidation of propylene through propylene oxide. Uses include antifreeze, resins and plasticizers, brake fluid, tobacco processing, food humectant, and preservative, pharmaceuticals, cosmetics, and inks. Production amounted to about 7,000,000 gallons for the fiscal year ended June 30, 1953. Other polypropylene glycols are produced, such as dipropylene glycol.

Glycerol (1,2,3,-Propanetriol, glycerin) is produced from treatment of fats in the soap making operations, synthetically from propylene via allyl chloride and allyl alcohol, and by fermentation. The major uses of glycerol are in alkyl resins, explosives, cellophane, and as a tobacco humectant. The production of glycerol in 1953 amounted to 218,000,000 lbs.

Pentaerythritol is made by condensation of acetaldehyde and formaldehyde. It is a solid and is used in producing synthetic resins; also (as the tetranitrate) in explosives. Production was 56,000,000 lbs. for the fiscal year ended June 30, 1953.

Sorbitol is produced by reduction of sugar, usually corn sugar, with hydrogen. It is a solid and is used as a conditioning or softening agent in paper, textiles, tobacco, glue and cosmetics, also as a source of alcohol in resin manufacture. It is used in foods, pharmaceuticals and for making other chemicals.

✓ *Cyclohexanol* may be prepared by catalytic hydrogenation of phenol or by catalytic air oxidation of cyclohexane. It is used as an intermediate in making adipic acid which in turn is employed in nylon manufacture; as a stabilizer and homogenizer for soap and synthetic detergent emulsions; as a solvent in the dye, textile and lacquer and resin industries; and in the preparation of other chemical compounds.

✓ *Benzyl alcohol* is usually manufactured from benzyl chloride and sodium or potassium carbonate; benzyl alcohol has also been prepared from benzyl chloride and other alkalis or alkali salts of fatty acids, by reduction of benzaldehyde, benzoic acid, and benzoic acid derivatives, from bromobenzene and formaldehyde, and from benzyl chloride and oxygen. Used for making esters for use in the soap, perfume, and flavor industries. Some esters are used in suntan lotions and medicinal preparations. It is also used as a solvent in inks, cosmetics and special coatings. Production for the fiscal year ended June 30, 1953 was 775,000 pounds.

Phenyl ethyl alcohol, produced mainly by

Friedel Crafts Synthesis from benzene and ethylene oxide, is used principally in perfumes.

Furfuryl alcohol, produced by reduction of furfural, is used as a resin former, solvent, principally in the resin industry, as a dispersant in textile printing, and for production of tetrahydrofurfuryl alcohol.

LAWRENCE C. BYCK, JR.

Physiological Aspects

The toxicity of the aliphatic alcohols is a narcosis (anesthesia) without cumulative features. Action is upon the central nervous system. Toxicity increases by a factor of about three times for each carbon atom added in an homologous series, due to increased lipoid-to-water distribution which favors alcohol entering the lipoids of the nervous system. However, the difference in toxicity between methyl and ethyl alcohols is less than for higher successive members of the primary series. Toxicity decreases somewhat in the series primary, secondary, tertiary alcohols. After there are some eight carbons in the molecule, low water solubility and low volatility reduce the toxic hazard of swallowing and of inhalation. The unsaturated alcohols are more toxic than the corresponding saturated ones, the difference between allyl and *n*-propyl alcohols being about thirty times. There are not great species differences among warm-blooded animals in response to the alcohols.

Irritating effects upon mucous membrane and respiratory tract increase in an homologous series until decrease in water solubility limits concentrations in body fluids. The unsaturated alcohols are much more irritating than their saturated analogs. A low concentration of allyl alcohol vapors can cause pulmonary edema and can incapacitate a man through the pain and temporary blindness of corneal injury. Permanent lost vision can result from a high concentration. The alcohols are not active skin sensitizers, and seldom cause dermatitis.

The alcohols enter the blood stream rapidly from the stomach at rates that are proportional to their water solubility. The vapors enter the blood stream through the lungs. They penetrate the intact skin, but only with the unsaturated alcohols is toxicity sufficient to make this route of entry a probable source of poisoning.

As soon as the primary saturated alcohols reach the liver, oxidation to aldehyde and carboxylic acid begins, and it proceeds at a constant rate, increasing with the length of the carbon chain. With methyl alcohol, further oxidation of formaldehyde and formic acid is very slow, accounting for the great danger of this alcohol. Accumulation of these oxidation products apparently accounts for the blindness from injuries to retina and optic nerve which is characteristic of methyl alcohol poisoning. With ethyl and higher primary saturated alcohols, oxidation of the carboxylic acid to carbon dioxide and water proceeds promptly, apparently in the muscles. The secondary alcohols are oxidized only to the ketones, and the tertiary alcohols are not oxidized in the body. The

manner in which the body handles unsaturated alcohols is not known.

Small amounts of the alcohols are excreted unchanged in the urine and as vapors from the lungs. A portion of the oxidation products may also appear in the urine, some being conjugated with glucuronic acid, and a portion is in the expired air. It is the experience of industrial hygienists and physicians that a workman inhaling 8 hours a day, every working day, the following concentrations of vapors (in p.p.m. by volume) is unlikely to be affected: methyl alcohol 200, ethyl alcohol 1000, isopropyl alcohol 400, *n* butyl alcohol 100, isoamyl alcohol 100.

Like any other anesthesia, the first action of a dose of ethyl alcohol is on the higher centers of the brain, with emotions, inhibitions, judgement, and mental clarity being affected. Increasing doses increasingly affect the central nervous system, decreasing muscular coordination, perception and reaction time. Loss of muscular control follows and the terminal stage is an anesthetic death from respiratory and circulatory arrest. Diuresis results early from action upon the pituitary. If the stomach is empty of food, alcohol starts to reach the blood stream one to two minutes after it is swallowed. Food in the stomach somewhat retards absorption. Oxidation in the liver starts at once and a man can oxidize about 8 grams an hour. The oxidation yields calories to the body, as with any food, somewhat more from alcohol than from carbohydrate, but less than from fat.

The severity of symptoms is proportional to the amount of unoxidized alcohol remaining in the blood stream. A level of 0.05 per cent ethyl alcohol in the blood is compatible with sobriety. Some people are intoxicated at 0.06 per cent and practically all at 0.20 per cent. The fatal level in the blood is from 0.3 to 1.3 per cent, and 6 to 8 grams per kilogram body weight taken at one time on an empty stomach is fatal to a man. The habituation of the chronic drinker consists in an acquired ability of brain cells to function in the presence of ethyl alcohol, not in a special ability to oxidize it. The social problem of ethyl alcohol in beverages is due to psychological and nutritional factors, not to toxicity. The symptoms of the chronic alcoholic are not chronic ethyl alcohol poisoning. They are nutritional in origin, due to vitamin deficiencies caused by obtaining calories from alcohol to the neglect of vitamin-containing foods.

HENRY F. SMYTH, JR.

Denatured Alcohol

Denatured alcohol was first produced in this country about 1906, following the enactment by Congress of the Denatured Alcohol Law. This law was passed in order to free industrial users of ethyl alcohol from excessive taxes and thereby promote the use of alcohol in industrial processes.

The Government exercises a very close control of alcohol production, denaturation, and use, through the Alcohol and Tobacco Tax Division of the Internal Revenue Service in the U. S. Treasury Department. Federal Industrial Alcohol Regulations #3 gives all details of the requirements.

Denaturation is accomplished by mixing the pure alcohol with small quantities of various chemicals or substances so as to render it unfit for beverage use. Formulas giving denaturants authorized and quantities required are set forth in the Appendix to Regulations #3.

Three classes of denatured alcohol are permitted to be manufactured: (1) specially denatured alcohol; (2) proprietary solvent; (3) completely denatured alcohol. All three can be used free of Internal Revenue Tax.

According to Internal Revenue Service report for the fiscal year ended June 30, 1953, the quantities of various classes of denatured alcohols produced are shown below:

1. Specially denatured alcohol 239,202,023 wine gallons
2. Proprietary solvents 21,500,000 wine gallons (approx.)
3. Completely denatured alcohol 626,773 wine gallons

As a matter of interest, during this same period, pure alcohol withdrawals from industrial alcohol plants and industrial alcohol bonded warehouses were as follows:

Tax free governmental use	18,600,000	wine gallons
Hospital, scientific and educational use	1,300,000	wine gallons
Total tax-free	19,900,000	wine gallons
Tax paid	12,400,000	wine gallons
Total pure use	32,300,000	wine gallons

The great majority of manufacturers who use any quantity of ethyl alcohol for industrial purposes use Specially Denatured Alcohol because the fifty formulas currently authorized by the Appendix to Regulations #3 give the user a broad choice and enable him to select that formula which best satisfies the specific requirements of his process. Regulations #3 requires each user to post bond, obtain a permit, keep records and comply with all the restrictions set forth. Two examples of formulas and uses authorized are quoted below from the Regulations:

A. "Specially Denatured Alcohol #36A"

Formulation: To every 100 gallons of ethyl alcohol add five gallons of ethyl acetate.

Authorized Uses: Solvent in manufacturing: Candy glazes. Solvent for chemical manufacturing and purification.

Pectin

Other food products

Crude drugs

Glandular products and digestive ferments

Vitamins and related products

Medicinal chemicals, including alkaloids

Miscellaneous drugs, including tablet manufacture

Raw material in manufacturing chemicals:

Vinegar

Acetic Acid

Ethyl Acetate

B. "Specially Denatured Alcohol #37"

Formulation: To every 100 gallons of ethyl al-

cohol add:

Forty-five ounces eucalyptol USP,

Thirty ounces thymol USP, and

Twenty ounces menthol USP.

Authorized Uses: Solvent in manufacturing toilet preparations:

Hair and scalp preparations

Bay rum

Face and hand lotions

Body deodorants and deodorant creams

Tooth paste and tooth powder

Mouth washes

Solvent in manufacturing pharmaceuticals:

External pharmaceuticals not USP or NF.

Antiseptic solutions, NF

Solvent in manufacturing miscellaneous products:

Disinfectants, insecticides, etc.

Sterilizing and preserving solutions

Cleaning preparations and purposes

Theater sprays and incense

Proprietary solvents are made by mixing Specially Denatured Alcohol (usually Formula #1) with small quantities of additional chemicals, such as ethyl acetate, methyl isobutyl ketone, methanol, rubber solvent and gasoline. Whereas the Alcohol and Tobacco Tax Division does not prescribe the chemicals or the quantities to be used, it is necessary for the manufacturers of Proprietary Solvent to obtain a permit to use the Specially Denatured Alcohol and to have his formulation approved. Compliance with Regulations #3 is necessary as to restrictions set forth, such as type of container and method of distribution.

Proprietary solvents are made from 190 proof as well as 200 proof alcohol. They are widely used for cutting and thinning shellac, and are used (usually in the anhydrous form) in lacquer, spirit varnish, and printing ink formulations. Another important use is for cleaning glass and metal parts and for use in alcohol lamps, stoves and torches. In many chemical processes where the denaturants are not objectionable, these solvents can be used for purifying, recrystallizing or supplying the ethyl group. The proprietary solvents are not approved for antifreeze use.

In completely denatured alcohol the ethyl alcohol is considered to be so thoroughly denatured that the possibility of restoration to pure alcohol is remote. The Regulations usually provide two or more formulas which when filled into approved packages may be used without Federal permit for any lawful purpose.

Formulation: To every 100 gallons of ethyl alcohol of not less than 160 proof add:

	CD 18	CD 19
Methyl isobutyl ketone	2.5 gals.	4 gals.
Pyronate or a similar compound thereto	.125 gals.	
Acetaldol (hydroxy-butyraldehyde)	.5 gals.	
Kerosene	1 gal.	1 gal.

Examples of general uses are: antifreeze, fuels,

paints, — varnishes, soaps, dipping fluids, dyes and stains.

LAWRENCE C. BYCK, JR.

Cross-references: *Glycerol, Glycols, Aliphatic Compounds, Antifreeze Agents*

ALDEHYDES

Aldehydes are members of an important class of organic compounds characterized by the presence of a carbonyl group ($\text{C}=\text{O}$). The name aldehyde



is derived from the fact that members of this series of compounds can be obtained when primary *Al*c*o*h*o*l*s* are *DEHYDrogenatEd* either by dehydrogenation or oxidation reactions. This indicates that aldehydes are intermediary between primary alcohols and acids, which are formed on further oxidation. Aldehydes are closely related to ketones, which also contain the carbonyl group, the difference being that aldehydes have at least one of the bonds from the carbon atom of the carbonyl group to a hydrogen atom, while with ketones each bond must be to some organic radical. Consequently the aldehyde group can occur only at the end of an aliphatic chain or attached directly to the aromatic or heterocyclic ring. As aldehydes are much more reactive than ketones, they require separate treatment. (See *Carbonyl Compounds*)

Physical Properties. The aldehyde group is an osmophilic group; thus the odor is often characteristic. The lowest members of the series are irritating and unpleasant but a pleasing odor develops with an increasing molecular weight, so that C_8 – C_{12} members are often used in synthetic perfumes. Also many of the pleasing, volatile oils of nature are higher molecular weight aldehydes.

The first member of the series of aldehydes is a gas at room temperature and pressure. The boiling points of succeeding members increase with the molecular weight. The first two members are miscible with water in all proportions, and in general solubility in water decreases with increasing molecular weight except where the presence of other groups within the molecule may influence it.

Nomenclature. Many common aldehydes are given nonsystematic names usually relating to their original source, such as vanillin, acrolein, cinnamylaldehyde, anisaldehyde, etc.; but chemically, they are usually named by one of two methods: (1) After the common name of the acid which it forms upon oxidation; the ending *-ic* or *-oic* of the acid is deleted and the word aldehyde is added, as for example in formaldehyde (which oxidizes to formic acid), acetaldehyde (which forms acetic acid), benzaldehyde (which forms benzoic acid), etc. (2) The I.C.U. system which names the aldehyde after the parent hydrocarbon with the longest continuous carbon chain containing the aldehyde group on the terminal carbon atom. The characteristic I.C.U. hydrocarbon ending *-ane* is deleted and the ending *-al* is added. Thus for example formaldehyde becomes methanal, acetaldehyde becomes ethanal, etc.

Preparation. Aldehydes can be prepared in the laboratory by a variety of methods. Many are applicable both to the aliphatic and aromatic series, but a few can be used only for aromatic aldehydes. The industrial procedure for the preparation of aldehydes is often quite different from that used in the laboratory. The exact procedure often varies with the aldehyde being produced.

(1) Mild oxidation of primary alcohols. This is often a difficult reaction to carry out, since the aldehyde formed is often more susceptible to oxidation than the alcohol from which it was formed. Thus oxidation may continue, with the resulting formation of the corresponding acid instead. (2) Hydrolysis of a dihalogen compound if both halogen atoms are on the terminal carbon atom. (3) Pyrolysis of a mixture of calcium formate and the calcium salt of the corresponding acid. (4) Treatment of an olefin with ozone, followed by hydrolysis with heat. (5) The Grignard reaction using an excess of ethyl formate. (6) Treatment of the corresponding acid halide with a mild reducing agent.

The following methods are applicable only to aromatic aldehydes:

(1) Mild oxidation of methyl side-chains attached to the aromatic ring (2) Gattermann-Koch procedure. Treatment of benzene or its homologs with a mixture of carbon monoxide, hydrogen chloride, cuprous chloride and aluminum chloride. A variation of this is the Gattermann procedure, which uses sodium cyanide in place of carbon monoxide and eliminates the cuprous chloride. (3) Reimer-Tiemann procedure for production of hydroxyaldehydes. Heating an aqueous, basic solution of a phenol with chloroform.

Reactions. Due to the presence of the reactive carbonyl group, aldehydes can be considered one of the more reactive series of organic compounds. The more important reactions can be conveniently grouped into six classes:

(1) *Oxidation.* Aldehydes are easily oxidized by mild oxidizing agents, and sometimes even by oxygen of the air alone, to form the corresponding acid. This ease of oxidation is often used as a means of detecting their presence, and differentiating them from the related ketones.

(2) *Reduction.* Aldehydes can be reduced catalytically or by any mild reducing agent to form the corresponding primary alcohol. The Cannizzaro reaction is an intermolecular oxidation-reduction limited to aldehydes with no hydrogen on the carbon atom adjacent to the carbonyl group. Two molecules of the aldehyde under the influence of sodium hydroxide form one molecule each of the corresponding alcohol and acid (See *Cannizzaro*).

(3) *Addition to the carbonyl oxygen.* (a) With water to form the unstable 1,1-dihydroxy derivative. The product is stable only in water solutions or with certain substituted aldehydes such as trichloroacetaldehyde to form the product known as chloral hydrate. (b) With ammonia to form the aldehyde-ammonia complex. The simple complex is unstable but readily polymerizes to form a stable, crystalline compound. (c) With alkali bisulfite to form a crystalline bisulfite addition product. (d) With hydrogen cyanide to form the important

cyanohydrins. (e) With alcohols to form first the hemiacetal and further to form the acetals. These are stable compounds derived from the unstable 1,1-dihydric alcohols. Aldehydes also react with the poly-alcohols such as polyvinyl alcohol to form useful resins.

(4) *Reaction with the carbonyl oxygen with loss of water.* (a) With hydroxyl amine to form the oxime. (b) With phenyl hydrazine and substituted derivatives to form the hydrazones. This reaction is used particularly in the identification of carbohydrates. (c) With semicarbazide to form the semicarbazone.

The above reactions are often used for the purification and/or identification of aldehydes, since all derivatives are crystalline products, easily purified, easily regenerate the aldehyde and most have definite melting points.

(5) *Polymerization.* (a) Aldehydes with an active hydrogen on the carbon adjacent to the carbonyl group undergo "aldolization" to form hydroxy aldehydes. With formaldehyde some of the hexose sugars have been isolated suggesting this as a possible mechanism for the formation of carbohydrates in nature. (b) Many of the lower molecular weight aldehydes form simple linear and cyclic polymers from which the monomeric aldehyde can be easily regenerated (see *Formaldehyde* and *Acetaldehyde* below). (c) Many higher molecular weight aldehydes form polymers of unknown structures (resins) under the influence of acids. This procedure can sometimes be used to differentiate aldehydes and ketones since the latter will not resinify readily. (d) Many aldehydes form useful resins when copolymerized with other molecules. See phenol- and urea-formaldehyde resins.

(6) *Miscellaneous reactions.* (a) With the Grignard reagent (RMgX) formaldehyde forms primary alcohols and all other aldehydes form secondary alcohols. (b) With phosphorus pentachloride to form the corresponding 1,1-dichloroderivatives by replacement of the carbonyl oxygen atom. (c) There are many other isolated reactions of lesser importance for example the Benzoin condensation, Perkin condensation, other condensations and other elimination reactions.

Acetaldehyde (Ethanal)

The second most important aldehyde from the commercial standpoint is acetaldehyde, over 224 million pounds having been produced in 1942. Total production figures for more recent years are not available. Acetaldehyde is an irritating liquid that boils at 22°C and is thus difficult to handle without refrigeration. The chief method of production is the hydration of acetylene in the presence of mercuric salts and a 6 per cent sulfuric acid solution. This process is feasible only when there is an abundance of cheap power for the production of acetylene. Acetaldehyde can also be produced by the mild oxidation of ethyl alcohol and is often recovered as a by-product in the first distillation in ethyl alcohol refineries.

Acetaldehyde, like formaldehyde, polymerizes readily. In the presence of sulfuric acid a liquid, cyclic trimer commonly known as paraldehyde is rapidly formed. When cold, an unstable solid

polymer known as metaldehyde is formed, but at room temperature this slowly decomposes to paraldehyde and acetaldehyde. From either polymer pure acetaldehyde is easily regenerated and is thus used as a convenient source of the pure monomer.

The chief use of acetaldehyde is as an intermediate in the production of other organic compounds, particularly in the catalytic conversion to glacial acetic acid, acetic anhydride, acetone, ethyl acetate, and vinyl acetate. Another important use is in the production of the compound known as aldol (butanol-3 al-1). This compound is easily dehydrated to crotonaldehyde (butene-2 al-1), which can then be hydrogenated to either butyraldehyde (butanal-1) or normal butyl alcohol (butanol-1). Other important uses are in (1) preservatives for fruit, (2) hardening of leather and other protein products, (3) organic syntheses, (4) in the production of resins and (5) dyes.

ELBERT H. HADLEY

Formaldehyde

Formaldehyde (CH_2O) is the unique first member of the series of aliphatic aldehydes. In the pure state, it is a colorless gas which condenses to a liquid at low temperatures (b.p. -19°C , f.p. -118°C). Both liquid and gas polymerize readily and can be kept in the monomeric state for only a limited time. It is readily soluble in water and is marketed chiefly as an aqueous solution although solutions in methanol, propanol and butanol have also been offered commercially. Considerable quantities are sold in the form of the solid, hydrated polymer, paraformaldehyde, $\text{HO} \cdot (\text{CH}_2\text{O})_n \cdot \text{H}$ or $(\text{CH}_2\text{O})_n \cdot \text{H}_2\text{O}$. Trioxane, $(\text{CH}_2\text{O})_3$ (m.p. $61-2^\circ\text{C}$, b.p. 115°C), the true cyclic trimer of formaldehyde, is also manufactured on a limited scale.

As a result of its chemical reactivity, high purity and low cost, formaldehyde has become an industrial product of outstanding commercial value. Production measured in terms of the 37% aqueous solution reached 1.02 billion pounds in the United States alone in 1952. Total U. S. production capacity is estimated as about 2.5 billion pounds for 1956.

Formaldehyde is produced principally from methanol, but appreciable quantities are also derived from the direct oxidation of hydrocarbon gases.

Two methanol processes are in use. In general, these procedures involve passing a mixture of methanol vapors and air over a stationary catalyst at approximately atmospheric pressure and scrubbing the off-gases with water to obtain aqueous formaldehyde. The first or classical procedure makes use of a silver catalyst and employs a rich mixture of methanol with air. The second method makes use of an oxide catalyst, e.g. iron-molybdenum oxide, and produces a formaldehyde solution which is substantially free of unreacted methanol.

Hydrocarbon oxidation processes for formaldehyde manufacture involve a controlled gas phase oxidation followed by abrupt cooling and condensation of the products. This is usually accom-

plished by scrubbing with water to yield a crude solution which must be refined to isolate formaldehyde from the other products. Formaldehyde is not the major product of these petrochemical processes. Other products include acetaldehyde, acetic acid, methanol, acetone, etc.

Standard commercial formaldehyde is a 37% by weight solution of formaldehyde in water containing sufficient methanol to prevent precipitation of polymer under ordinary conditions of shipping or storage. Methanol concentrations range from 6 to 15% according to trade requirements. This solution is known as the U.S.P. grade. Low methanol solutions containing 1% or less methanol are also marketed and contain 37%, 45% or 50% formaldehyde. These solutions must be kept warm to avoid separation of polymer and can be shipped only in insulated tanks. Formaldehyde is hydrated by water and the aqueous solution contains an equilibrium mixture of the monohydrate methylene glycol, $\text{CH}_2(\text{OH})_2$, and polyoxymethylene glycols, such as $\text{HOCH}_2\text{OCH}_2\text{OH}$ and $\text{HO}(\text{CH}_2\text{OCH}_2\text{OCH}_2\text{O})_n\text{H}$. As a result the partial pressure of formaldehyde is quite low (about 1 mm at 20°C).

Formaldehyde has a pungent odor and its solutions and vapors are highly irritating to the mucous membranes of the eyes, nose and upper respiratory tract. The maximum allowable concentration of formaldehyde vapor in air, as generally accepted, has been set by the American Standards Association at 10 ppm by volume (1944). This concentration is conceded as allowable for exposures not exceeding 8 hours daily. Contact of solution with the skin should be avoided since it causes hardening or tanning, diminished secretion and, in some cases, leads to dermatitis.

Paraformaldehyde is usually produced by vacuum concentration of the aqueous solution until a solid containing 91% or more formaldehyde is obtained. The 95 to 96% product is probably the most familiar grade. It evolves formaldehyde gas and should be handled with essentially the same precautions as the solution.

Formaldehyde has a high degree of chemical reactivity and will combine chemically with almost every type of chemical compound. It reduces to methanol and oxidation gives formic acid or carbon dioxide and water. In aqueous solutions, the Cannizzaro reaction yields formic acid and methanol in equimolar proportions: $2\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{CH}_3\text{OH}$. This reaction accounts for the gradual increase in acidity of commercial solutions on storage. Formaldehyde also undergoes an aldol-type condensation yielding hydroxy aldehydes, hydroxy ketones and hexose sugars. This reaction, which is autocatalytic, is usually initiated under alkaline conditions.

Formaldehyde forms methylol (hydroxymethyl), $-\text{CH}_2\text{OH}$, or methylene ($=\text{CH}_2$) derivatives on reaction with most organic chemicals. Resins are produced by polycondensations in which reactant molecules are linked by methylene groups.

In the presence of acid catalysts formaldehyde combines with alcohols, glycols and other polyhydroxy compounds to form the formaldehyde acetals or formals, $\text{CH}_2(\text{OR})_2$. Unstable hemi-

acetals (HOCH_2OR) are produced under neutral or alkaline conditions. Reaction of formaldehyde with alcohols and hydrogen chloride gives alpha chloromethyl ethers (ROCH_2Cl). Dichloromethyl ether ($\text{ClCH}_2\text{OCH}_2\text{Cl}$) is produced by the action of hydrogen chloride on paraformaldehyde in cold concentrated sulfuric acid.

Aldehydes and ketones containing alpha hydrogen atoms react with formaldehyde to give mono- and polymethylol derivatives under alkaline catalysis followed by reduction of the carbonyl group in some instances. This is exemplified by the production of pentaerythritol [$\text{C}(\text{CH}_2\text{OH})_4$] from acetaldehyde and formaldehyde. Phenols form nuclear methylol derivatives (phenol alcohols) which undergo polycondensation to form the methylene-linked phenol-formaldehyde resins.

Ammonia condenses with formaldehyde to form hexamethylenetetramine and the related methylene amines with primary and secondary amines. Methylamines are formed by acid condensations with ammonia and amines. Amides react to form methylol derivatives and polycondensation products such as the urea-formaldehyde resins.

Unsaturated and olefinic hydrocarbons react with formaldehyde in the presence of strong acids. Reactions with olefins (Prins Reaction) give 1,3-glycols or derivatives of these products. Methylene linked products are obtained with aromatics. The formation of chloromethyl derivatives, such as benzyl chloride from formaldehyde, hydrogen chloride and benzene, offers a valuable method of synthesizing aromatic compounds. Acetylene reacts with formaldehyde in the presence of copper acetylide to give butynediol ($\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$).

The principal use of formaldehyde is in the manufacture of the phenol, urea and melamine resins. Large volumes are also employed in the synthesis of hexamethylenetetramine, pentaerythritol, ethylene glycol (ex formaldehyde, carbon monoxide and hydrogen), sulfoxylate reducing agents (by hydrogenation of the aldehyde bisulfite compounds), phenyl glycine for manufacture of indigo, etc. Plastics and synthetic fibers are also produced by the resinification of proteins such as casein, soybean protein, etc. In the textile industry, formaldehyde is used alone or more commonly in combination with urea or melamine to improve shrink and crease resistance of rayon fabrics. Similar applications in the paper industry improve wet strength and shrink resistance of paper products. Leather and fur can be tanned by the action of formaldehyde and its derivatives.

Direct uses of formaldehyde as a bactericide, disinfectant and embalming agent, although once major applications, now consume only a small proportion of this versatile chemical. Disinfection of seeds and soil in agriculture prevents smut, scab and other plant diseases. Formaldehyde is also an acid inhibitor and has shown value in preventing the sulfide corrosion of oil-well equipment.

J. FREDERIC WALKER

Cross-references: *Phenolformaldehyde Resins, Noxious Gases*

ALICYCLIC AND CYCLIC COMPOUNDS

Compounds having three or more atoms joined to form a closed ring are known as cyclic compounds. Cyclic compounds with properties resembling those of aliphatic compounds of the same functional type, rather than those of aromatic compounds, are termed alicyclic compounds. This term strictly applies to both the carbocyclic type, in which all the ring atoms are carbon, and to the heterocyclic type, having other than carbon atoms in the ring. In practice, however, the term is usually limited to carbocyclic compounds. These compounds have received a great deal of attention because of their widespread occurrence in nature and their commercial and theoretical importance.

The simplest alicyclic, cyclopropane, is prepared by the reaction of zinc dust with trimethylene chloride. It is frequently used as an anesthetic in surgery. Cyclohexane is prepared by catalytic hydrogenation of benzene and is a commercial solvent. Cyclohexanol, obtained by hydrogenation of phenol, is an intermediate in the synthesis of nylon. Addition of chlorine to benzene gives a mixture of the isomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexane, which is the valuable insecticide, lindane or gamma-hexane. Ethylene oxide, an alicyclic with a hetero atom, is a very reactive compound, useful in many synthetic processes.

Cyclopentane, cyclohexane and their methyl derivatives occur in petroleum. The potent insecticide pyrethrin I occurs in pyrethrum flowers; muscone is the odoriferous principle of musk and important in perfumery. α -Pinene is the chief constituent of turpentine oil. Another terpene, camphor, has long been valued in medicine and has found much use in the manufacture of "Celluloid." Naturally occurring polycyclic representatives include triterpenes such as abietic acid (pine rosin) and steroids such as cholesterol (widely distributed in the animal body).

The chemical properties of alicyclic compounds are affected so much by ring size that it has been found convenient to classify them in this manner: (a) Small rings of three and four members, which are relatively difficult to form and are most reactive; (b) common rings of five to seven members, which are usually readily formed and are very stable, like open-chain aliphatic chains; (c) medium rings of eight to twelve members, which are difficult to synthesize by most methods but are generally stable, and in which class ordinary reactions may occur in an abnormal "transannular" manner; and (d) large rings (or macrocyclics), having more than 12 members, which also are difficult to synthesize but once formed are very stable. The chemical properties of functional groups on alicyclic rings are also affected by the ring size; for instance, small rings seem abnormally electronegative.

An ingenious explanation for the effect of ring size on the reactivity of alicyclic rings was proposed by Baeyer in 1885 and is famous as the "strain theory." It is based on two assumptions: (1) that the carbon atoms in any alicyclic ring are coplanar, and (2) that the bonds of a tetra-substituted carbon atom are normally at the tetra-

hedral angle of $109^{\circ}28'$, but that this angle can be altered. Any deviation of this angle, however, is considered to result in a condition of internal strain in the molecule, decreasing its stability and causing it to be more difficult to form. The strain was measured as one-half of the difference between the tetrahedral angle and the actual angle.

EFFECT OF RING SIZE ON RING STRAIN

No. atoms in ring	Bond Distortion	Heats of Combustion kcal./CH ₂ group
2	$54^{\circ}44'$	
3	$24^{\circ}44'$	168.5
4	$9^{\circ}44'$	165.5
5	$0^{\circ}44'$	159
6	$-5^{\circ}16'$	158
7	$-9^{\circ}51'$	158
8	$-12^{\circ}51'$	
9	$-15^{\circ}16'$	
10	$-23^{\circ}16'$	158.5

For 3-, 4- and 5-membered rings, the size of the bond angle distortion does indeed parallel the reactivity of the ring system and the theory can be extended successfully to ethylene, if it is considered to have a 2 membered ring. Thus hydrogen adds to ethylene with a nickel catalyst at 40° ; under such conditions 100° is required for hydrogenolysis of cyclopropane, 180° for cyclobutane and 300° for cyclopentane. Cyclopropane adds bromine and iodine to produce 1,3-dihalopropanes, and hydrogen bromide and hydrogen iodide to form the 1-halopropanes, while the larger rings are inert toward such reagents under usual conditions. Cyclopropyl ketones, acids and esters are capable of undergoing conjugate addition with active methylene compounds, and their ultraviolet spectra indicates that the cyclopropyl group can conjugate with a carbonyl group, like an olefinic double bond. Small ring compounds containing a hetero atom in the ring also show an unusually high reactivity. The 3 membered rings are more reactive than the 4-membered, and some, like ethylene oxide, are very important reagents in organic synthesis.

The latest modification of the "strain theory" for small rings is that the direction of bonding of the carbon atoms remains at the tetrahedral angles, but that the bonds are bent. This results in less than the maximum overlap of the bond orbitals in the ring and therefore weaker bonds than normal.

Baeyer's prediction that cyclopentane would be easily formed and stable was quickly confirmed by its synthesis and the determination of its properties. This work also showed, however, that cyclopentane and cyclohexane are of nearly equal stability. Precise work done later on heats of combustion showed that the cyclohexane ring is actually slightly more stable than the cyclopentane ring, and the larger rings are also approximately strainless.

Since Baeyer's strain theory pictured cyclohexane as more strained than cyclopentane, and greater strain was associated with the larger rings, due to the assumption that all rings were

coplanar this part of the theory had to be modified. It was recognized that rings of 6 members and higher were not planar but puckered, to allow the normal tetrahedral angle between the carbon atoms. Cyclohexane thus can exist in two modifications: a "chair" form and a "boat" form (referring to the shape of the structural formulas). There is apparently an equilibrium between them, the former predominating. As a consequence of this there are two kinds of hydrogens in cyclohexane: the ones above and below the carbon skeleton being known as axial (a) and those around its periphery as equatorial (e). Substituents also can occupy either axial or equatorial positions, with the result that different conformations of the same "isomer" are possible of course, the conformation with minimum internal repulsive forces is favored in such cases.

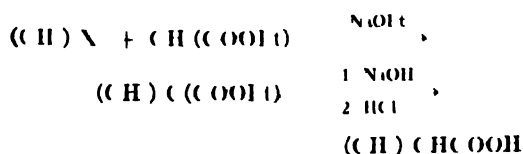
Recent spectral studies have shown that cyclopentane and even cyclobutane are also somewhat puckered. Apparently repulsive forces between hydrogen atoms causes the carbon atoms to twist so as to stagger the hydrogen atoms on adjacent methylene groups, and thus increase H-H distances. In rings of 8 to about 12 members the puckering causes some atoms which are not bonded to each other to be in very close proximity, resulting in some π - π discovered transannular reactions. Thus, hydrolysis of 1,2-epoxycyclooctane gives rise to 1,4-cyclooctanediol as well as the expected 1,2 isomer, apparently due to an intramolecular hydride ion shift. Likewise oxidation of cyclononane gives 1,5-cyclononanediol and that of *cis*-cyclodecane gives 1,6-cyclodecanediol. These medium rings appear to be slightly strained because of the closeness of some of the nonbonded atoms, but when the ring size is increased further the ring becomes strainless, loose structures which tend to "collapse". X-ray spectral data indicate, for example, that a ring ketone of more than 16 carbon atoms resembles a double paraffin chain joined to a carbonyl group.

There is a marked effect of ring size on ease of formation of alicyclic compounds, although it is not parallel to ring stability. Generally 5- and 6-membered rings are most easily formed, and large rings of 10 to 12 members are the hardest to form. At this size the two ends of the coiled carbon chain apparently are least likely to collide because the other atoms in the chain get in the way. It is somewhat easier to close a 3-membered ring than a 4-membered one, proximity thus appearing more important than deformation of bond angles.

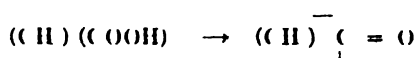
Some general methods of synthesis of alicyclic compounds are:

(1) Freund synthesis from dihalides: $(\text{CH}_2)_n \text{X}_2 + \text{Zn} \rightarrow (\text{CH}_2)_n + \text{ZnX}_2$

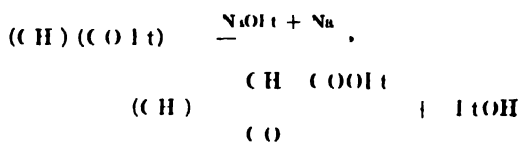
(2) Malonic and acetoacetic ester methods, for example



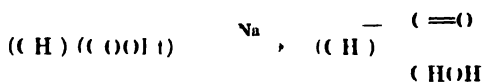
(3) Thermal decarboxylation of dicarboxylic acids or their salts giving cyclic ketones



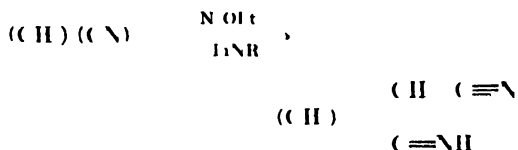
(4) Dieckmann reaction (mainly for 5- and 6-membered rings)



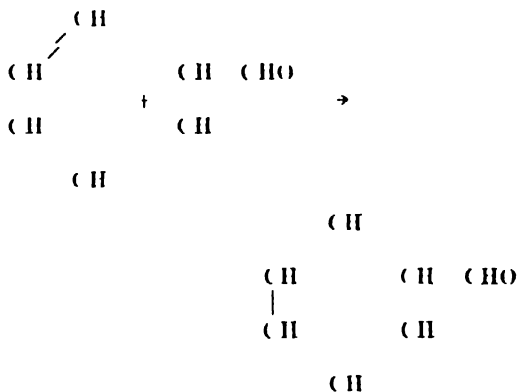
(5) Acyloin condensation (best for large rings)



(6) Thorpe reaction (good with large rings)



Particularly valuable in the synthesis of 6-membered rings are the diene synthesis and hydrogenation of aromatic compounds

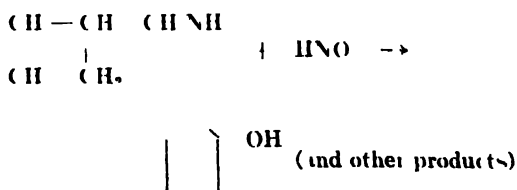


Methods for going from one ring size to another are of importance such as

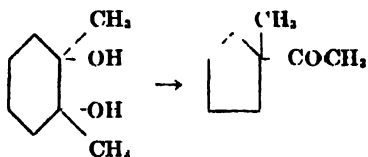
8. Ring enlargement of cyclic ketones with diazomethane



(9) Demjanov ring expansions and contractions



(10) Pinacol-pinacolone rearrangement:



DR. SCOTT SEARLES, JR.

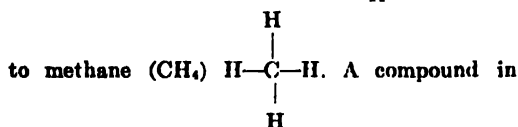
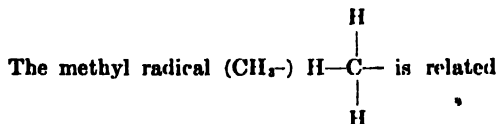
Cross-references: *Aliphatic Compounds, Aromatic Compounds, Heterocyclic Compounds*

ALIPHATIC COMPOUNDS

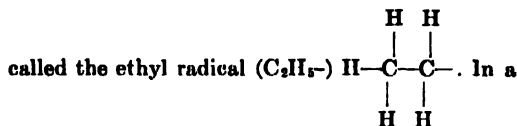
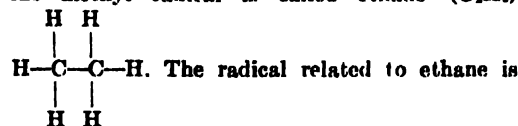
Organic compounds characterized by open chain structures are called aliphatic; contrasted with these are aromatic compounds, which have ring structures. Aliphatic compounds as a class are named from the Greek word *aleiphar*, which means fat or oil. While it is true that fats and oils are included among the aliphatic compounds, the group is far larger than fats and oils alone. All open-chain hydrocarbons, both saturated and unsaturated, are aliphatic compounds. Also all esters, ethers, ketones, aldehydes, amines, amides, alcohols, carbohydrates, and substitution products of all the groups mentioned are aliphatic compounds, provided that they have no ring structure.

Hydrocarbons contain carbon and hydrogen only; those that contain the maximum possible quantity of hydrogen are called *saturated* hydrocarbons. Saturated hydrocarbons are thought to contain bonds between adjacent carbon atoms that consist of a single shared electron pair (covalent bond). Saturated hydrocarbons all burn in air or oxygen. When the supply of air is adequate, the products of burning a hydrocarbon are carbon dioxide and steam (water). Saturated hydrocarbons do not combine readily with bromine or with halogen acids. Their chemical activity, aside from the ability to burn, is in general small.

Methane (CH_4) is the simplest and most abundant hydrocarbon. It is the chief constituent of natural gas. Methane (b. p. -161.5) is thought to have a tetragonal molecule in which all the hydrogen atoms are spaced an equal distance from the carbon atom and an equal distance from one another.



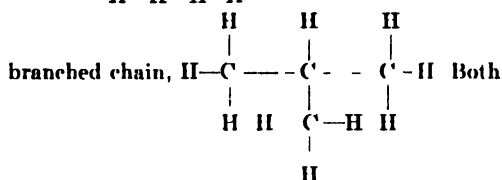
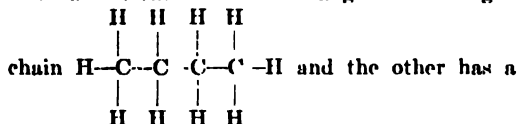
which one hydrogen of methane is replaced by the methyl radical is called ethane (C_2H_6)



similar manner, the propyl radical ($\text{C}_3\text{H}_7\cdot$) is related to propane (C_3H_8) and the butyl radical ($\text{C}_4\text{H}_9\cdot$) to butane (C_4H_{10}).

As the number of carbon atoms increases, the molecular weight of the compounds in this the paraffin series increases, the boiling point rises, the specific gravity increases, but the general chemical properties are substantially the same. Pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}), nonane (C_9H_{20}), and decane ($\text{C}_{10}\text{H}_{22}$) all correspond to the general formula $\text{C}_n\text{H}_{2n+2}$.

We can represent two formulas for butane. One has the carbon atoms arranged in a straight



arrangements correspond to the formula C_4H_{10} . Corresponding to these two formulas, two different butanes, and only two, are known. The straight-chain butane (normal butane) boils at -0.6° , and the branched chain compound (isobutane) boils at -10.2° . These compounds are isomers of one another, that is, they differ in structure, but not in composition. Their properties differ slightly. As the number of carbon atoms increases, the number of isomers increases greatly. For example, nonane has 35 isomers.

Unsaturated hydrocarbons are called alkenes if they have one double bond, alkadienes if they contain two double bonds. Unsaturated hydrocarbons that have a triple bond are called alkynes. Saturated hydrocarbons, on the other hand, are called alkanes. A double bond represents the bonding force between two adjacent carbon atoms as being attributed to two covalent electron pairs; a triple bond represents three covalent electron pairs between adjacent carbon atoms. Double and triple bonds do not represent additional bonding force, however; on the contrary, they are points for chemical attack on the molecule. For example, one mole of a hydrocarbon that contains one double bond reacts with one mole of bromine. One mole of a hydrocarbon that contains a triple bond reacts with two moles of bromine.

Propane (C_3H_8) is a typical alkane. It is found in petroleum and in natural gas. It is also a by-product of the refining of petroleum. It boils at -42°C , and is a gas at room temperature. Huge quantities of this gas are used for rural domestic fuel gas.

Ethylene (ethene) (C_2H_4) is the simplest alkene.

It is found in natural gas, and is made to some extent by the destructive distillation of coal or wood; it is also formed by cracking petroleum. It may be made by dehydration of ethanol and by several other methods. Like all hydrocarbons, ethylene burns. It also undergoes a number of reactions that depend upon addition to the double bond. Chlorine, bromine, halogen acids, hypochlorous acid, hydrogen, and ozone all add characteristically at the double bond. Ethylene also polymerizes to form the well-known plastic material, polyethylene.

Butadiene is a well-known example of an alkadiene. 1,3 Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) contains alternate double and single bonds, an arrangement called a conjugated system. Isoprene [$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$] is closely related to butadiene. Butadiene may be obtained by distilling natural rubber. Isoprene is used in the synthesis of synthetic elastomers. (See *Butadiene*.)

Acetylene (C_2H_2) is the simplest and best known member of the alkyne series. It contains a triple bond ($\text{HC}\equiv\text{CH}$), and it is correspondingly more reactive than ethylene. Acetylene is made in great quantities from the reaction of calcium carbide with water: $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2\uparrow + \text{Ca(OH)}_2$. The gas is stored in tanks that contain porous material and acetone. Otherwise the gas may explode when it is compressed. Acetylene burns with an exceedingly hot flame which has the combined effect of the heat of decomposition and the heat of combustion. The well known oxy-acetylene torch uses this gas for fuel. Acetylene is also an important raw material for several syntheses. (See *Acetylene*.)

Alcohols are related to hydrocarbons in that one or more of the hydrogen atoms is replaced by an OH group. Ethanol or grain alcohol is manufactured by the fermentation of grain. Today, however, more than one half of the supply of ethanol ($\text{C}_2\text{H}_5\text{OH}$) is made by processes that consist essentially of adding the elements of water to the double bond of ethane, $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH}$. (See article on *Alcohols* for complete discussion.)

Ethers are organic oxides. If R represents a hydrocarbon radical such as methyl (CH_3), ethyl (C_2H_5) or vinyl ($\text{CH}=\text{CH}_2$), then ROH is an alcohol and $\text{R}-\text{O}-\text{R}'$ is an ether. Diethyl ether is the ether most frequently used. It is made by dehydration of alcohol. It is well known as a solvent, fuel, anesthetic, and medium for organic reactions. Ethers that have two different substituents for R are called mixed ethers. Diethyl ether ($\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$) is not a mixed ether, but methyl ethyl ether ($\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$) is called a mixed ether. (See article on *Ethers* for complete discussion.)

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Aldehydes have the group $-\text{C}(=\text{O})-\text{H}$. The general formula for an aldehyde is RCHO , and the simplest member of the aldehyde class is formaldehyde (HCHO). Like many other compounds that have hydrogen instead of a hydrocarbon radical for R, formaldehyde is not quite typical of the entire group of aldehydes. Perhaps acetaldehyde

(CH_3CHO) is more closely a typical compound. Aldehydes as a group are midway in oxidation condition between an alcohol and an organic acid. That is, oxidation of an aldehyde produces an acid; reduction of an aldehyde produces an alcohol. (See article on *Aldehydes* for complete discussion.)

Ketones are $\text{R}-\text{CO}-\text{R}'$. Again both mixed and simple ketones are known, depending upon whether the substituent for R is different or the same. $\text{CH}_3-\text{CO}-\text{CH}_3$ is dimethyl ketone, more commonly called acetone. Likewise, the R substituent may be a saturated or an unsaturated hydrocarbon radical. Acetone boils at 56.5°C . It is a colorless liquid that has a characteristic pungent penetrating somewhat sweet odor. It mixes completely with water and with gasoline. It is used as a solvent, and as a starting material in chemical syntheses. (See *Ketones*.)

Amines (RNH_2 , $\text{RR}'\text{NH}$, $\text{RR}'\text{R}''\text{N}$) and amides (RCONH_2 , $\text{R}'\text{CO RCONH}$, $\text{R}''\text{CO R}'\text{CO RCON}$) are derivatives of ammonia. (See article on *Amines* for complete discussion.)

Organic acids (RCOOH) are characterized by the carboxyl group. Formic acid (HCOOH), a liquid that boils at 100.7°C , is slightly atypical. Acetic acid (CH_3COOH) is a more typical member of the so-called fatty acid series. The members of this series with larger numbers of carbon atoms, such as stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$), are found in natural fats and oils in esters. Acetic acid is found in vinegar. It is made by fermentation of sugar followed by oxidation of alcohol, by destructive distillation of wood, and synthetically from ethanol or acetylene. Acetic acid is a weak acid, but it forms many well-known salts such as those of sodium, calcium, copper (the basic acetate), and lead. Acetic acid finds many uses in the arts such as in dyeing and in photographic work. It is used to make cellulose acetate, widely employed as a base for photographic film and for other purposes. One type of rayon (Celanese) uses acetic acid in its manufacture. (See *Acids*.)

When an acid and an alcohol react in the presence of a dehydrating agent, a compound called an *ester* may be formed in addition to water. For example, $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5$ (ethyl acetate) + H_2O . Esters have the general formula RCOOR' , and there are many possibilities. Theoretically, every alcohol and every acid should form an ester. Since mono-, di-, and trihydroxy alcohols are known, and since mono-, di-, and tricarboxy acids are known, the possible combinations are numerous. Esters often have a fragrant odor. Many of them are found in the flavors of fruits and flowers. Ethyl acetate boils at 77°C . It is a colorless liquid, slightly soluble in water, but miscible in all proportions with alcohol. It is a solvent, but somewhat toxic.

In many cases a hydrogen atom can be replaced by a halogen atom, the nitro group, or a similar element or radical. The resulting compound is still open-chain, hence aliphatic. Familiar examples are trichloroacetic acid (CCl_3COOH), chloroform (CHCl_3), carbon tetrachloride (CCl_4), and nitromethane (CH_3NO_2).

Still another large group of aliphatic com-

pounds is the *carbohydrates*. These include starches and sugars. The general formula is $C_6H_{12}O_6$. Common table sugar (sucrose, $C_{12}H_{22}O_{11}$) is the most familiar example of a carbohydrate. Glucose, corn sirup ($C_6H_{12}O_6$), and lactose in mammalian milk ($C_{12}H_{22}O_{11}$) are other examples of carbohydrates.

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Cross-references: *Hydrocarbons, Alcohols, Paraffins, Ethers, Aldehydes, Ketones, Amides, Amines, Fatty Acids, Esters, Carbohydrates, Fischer Tropsch Process, Butadiene*

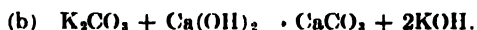
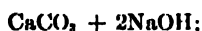
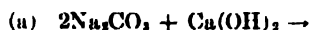
ALKALIES

Alkali is a name first applied to water-soluble components of the ashes of plants. Land plants furnish largely potassium carbonate (K_2CO_3), and sea plants, sodium carbonate (Na_2CO_3). The characteristic action of these extracts is their ability to neutralize acids, or in the absence of acids to establish a basic condition. The alkali metal family of the periodic table received its name because the hydroxides and carbonates of its members are alkalies.

In its broadest sense the term "alkalies" is used to designate not only the hydroxides and carbonates of all members of the alkali family, but also the hydroxides and carbonates of Ba, Ca, Sr, Mg and NH_4^+ , and some alkaloids. In its narrowest sense, the word may be used interchangeably with "soda ash," which is essentially Na_2CO_3 , because considering cost, abundance, availability, purity and ease of application, soda ash is the alkali most suitable for use in industry.

Alkalies are required in many industries among which are: glass, soap, chemical manufacture, cleaners, petroleum drilling and refining, pulp and paper, rayon and other textiles, reclaiming rubber, vegetable oils, and water treatment. Lye, $NaOH$; lime, CaO ; soda ash, Na_2CO_3 ; and ammonia, NH_3 are sold as comparatively pure alkalies in carload lots. In many cases the metal of the alkali becomes a part of the product, as in glass, soap and manufacture of chemicals. In such cases the alkalies may not be interchanged. In other cases the only function of the alkali is to decrease the acidity; here only the capacity to neutralize acid and the cost may need to be considered. For neutralization of acids, the relative costs of some common alkalies are: lime, 1.0; liquid NH_3 , 4.0; Na_2CO_3 , 4.1; $NaOH$, 5.9; and KOH , 33.0.

Sodium carbonate and potassium carbonate are the essential components of water extracts of plant ashes and were the mild alkalies of the ancients. Either of these is powerful enough as a base to produce soap by boiling with fats and oils. But in the distant past before records became reliable it was found possible to prepare more active substances, the caustic alkalies. These were made by adding the proper amount of lime to the water extracts of plant ashes. The reactions are essentially:



The $CaCO_3$ is insoluble; and $NaOH$ (caustic soda or lye), or KOH (caustic potash) remains in solution.

Today most of the caustic soda (sodium hydroxide) produced is made by electrolysis of brine (sodium chloride solution) using electrolytic cells. (See *Chlorine*).

Some lakes without outlets (usually in desert areas) contain Na_2CO_3 , and beds of impure Na_2CO_3 , or trona [$Na_2CO_3 \cdot NaHCO_3$] are found. These, too, are usually far from centers of population, such as Owens and Searles Lakes in the California desert. It is generally cheaper to manufacture any desired alkali than to gather and transport these natural products.

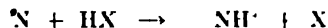
F. E. BROWN

Cross-references: *Alkaloids, Ammonia, Calcium, Potassium, Sodium*

ALKALOIDS

The nitrogen-containing bases found in plants are called alkaloids, a name meaning "alkali like." Alkaloids are widely distributed in nature coming from many genera and species of plants. The part of the plant from which a given alkaloid may be isolated is also varied; alkaloids have been found in leaves, roots, seeds, or bark, depending on the plant or the alkaloid of interest. Since the beginning of recorded history, alkaloids have attracted attention because of their pronounced and often fatal physiological activity, but it has been their basicity which has allowed them to be isolated readily from their natural sources, and identified as specific organic compounds.

The general method for isolation of alkaloids from plants is based on the fact that pure alkaloids are soluble in water immiscible solvents (ether, chloroform), while reaction with water



converts the alkaloid to its acid salt, which is soluble in water. To prepare a pure alkaloid, therefore, ground roots or leaves are first extracted with a solvent such as ether or chloroform until the residue is clear of extractable matter. The extract is then acidified with mineral acid, to cause precipitation of the acid salts. A thorough washing of the ether extract with acidified water takes the alkaloid into aqueous solution. Careful neutralization of the acid causes reprecipitation of the pure alkaloid, which may be recrystallized from a solvent in which it is sparingly soluble, such as acetone or methyl alcohol. Pure alkaloids prepared in such a manner as this are nearly all white crystalline compounds of fairly high melting points. They contain nearly every nitrogen-bearing heterocyclic ring system known, from the simple five-membered ring of hygrine to the complex fused ring system of yohimbine.

Chemically, alkaloids have two important properties different from other organic systems. The first

is their basicity, which is important in separating them from the mixtures in which they occur in nature. The other is that they all contain nitrogen, usually in a ring structure of some kind. This fact has been most important to investigators of alkaloid structure since the beginning of organic chemistry, about 1800. The well-known Hofmann degradation reaction, which by conversion of nitrogen to its quaternary hydroxide leads eventually to ring scission, has been a most valuable tool in this work, because it usually leads to readily identifiable fragments of the original compound. Other techniques which have been useful for structure determinations are hydrolysis of ester and amide linkages, oxidation, and alkaline fusion, all of which break up alkaloid molecules into more readily identifiable fragments.

Another chemical property which must be mentioned, but which is not unique for alkaloids, is optical rotation. Because alkaloids are naturally occurring compounds, they are produced as pure optical isomers. For example, the primary alkaloid of tobacco, nicotine, is levorotatory, while the optical configuration of *d*-nor nicotine, a closely related compound found in a different plant, has the opposite optical configuration. Quite frequently it has been found that a given alkaloid has certain physiological actions completely absent in its mirror-image alkaloid, which differs only in the configuration about one carbon atom.

The systematic organic names for most alkaloids are long and unwieldy, and as a result they all have common names by which they are known in commerce and medicine. Alkaloids are usually named for the genus or species of plant from which they come, such as pilocarpine (*Pilocarpus jaborandi*), nicotine (*Nicotiana tabacum*), and harmaline (*Peganum harmala*), but many are named for different reasons. Some are named for physiological effects, such as emetine (an emetic) and morphine, a soporific. The pomegranate alkaloids, pelletierines, are named after the early investigator of alkaloids, the French chemist Pelletier, who isolated strychnine in 1818, and quinine in 1820.

A given species of plant often contains more than one alkaloid, although they are usually quite closely related in structure. Thus, *Hydrastis canadensis* contains both hydrastine and berberine. It also happens that a species contains only one alkaloid. Thus far the species *Colchicum* has yielded only a single alkaloid, colchicine.

Alkaloids are thought at present to occur in plants as either starting materials or side products from the biosynthesis of proteins. Alkaloids occur in the rapidly growing parts of plants (seeds) or in the dead parts (bark) facts which lend support to this belief. Also, some alkaloids show remarkable similarity to simple amino acids. For example, ergotamine from ergot can be thought of as made from four simple amino acids, lysergic acid, α -hydroxyalanine, phenylalanine, and proline. It must be added that this is not the whole story; some alkaloids have the sterol structure (solanidine and veratrum alkaloids) while others show no obvious relation to any other biologically active compound.

Alkaloids have attracted attention through the centuries not from their chemical properties but rather from their physiological activity. The poisoning of arrows, the chewing of betel nut, and the smoking of tobacco all have their basis in the specific action of an alkaloid. In South America, the Indians have long poisoned their arrows with curare, a mixture which contains curine as the principal alkaloid. Chewing betel nut and smoking tobacco are both done for stimulation, and the alkaloids providing the stimulation are arecoline and nicotine. Some of the more potent alkaloids are also habit-forming, and their use is strictly regulated, but they are still among our most beneficial drugs. Strychnine, a violent poison in overdose, can be successfully used as a heart stimulant in extreme cases. Morphine and cocaine, infamous for their tendency to become habit-forming, are two of the most effective analgesics known to medicine. Other alkaloids common in medical practice are quinine, an antimalarial, and colchicine, used sometimes in treatment of gout. The reserpine alkaloids have recently shown some promise in treatment of mental disease and hypertension.

Alkaloids are marketed as crude drugs. Their potency depends greatly on the age of the plant, the time of year harvested, the duration of storage, and the method of preparation. Also, the mixture may or may not contain harmful adulterants. As a result, each batch of drug must be checked by costly and time-consuming biological assay before it can be placed on the market. To avoid these difficulties, organic chemists early tried to prepare pure alkaloids by synthetic means. They have been outstandingly successful in their task, having prepared nearly all the simpler ones, (harmaline, tropine) and some of the more complex ones, such as papaverine. Along the way, chemists have developed many substitutes for the natural drugs. Quite often the substitute has the beneficial properties of the natural drug, with fewer deleterious side effects. For example, procaine (Novocaine), has largely replaced cocaine as a local anesthetic; it is about one half as potent as an anesthetic, but only one-fourth as toxic. Demerol has proved useful as a substitute for morphine. Also many antimalarials have been developed to replace quinine. In spite of all these recent developments, natural alkaloids are still among the most useful medicines we have, and some of the ring systems which nature puts together with such surprising ease may continue to baffle chemists for years to come.

ELBERT C. WEAVER

Veratrum Alkaloids

The veratrum alkaloids are a group of alkaloids containing a steroid like ring systems and occurring in certain members of the *Liliaceae* family. They are of particular interest because of their activity in lowering blood pressure and certain of them are used clinically for this purpose. This hypotensive activity, which is most pronounced among the triesters, is about half as great among the di- and tetra-esters, about 1/20th as great among the mono esters, very low among the glycosides and almost lacking among the alkalamines.

The intravenous hypotensive dose for the anesthetized dog is of the order of 1 microgram per kg. body weight and the oral hypotensive dose for the human being is of the order of 0.4 to 1 mg., using protoveratrine A in both cases. Accompanying the lowering of blood pressure, there is a slowing of heart rate and occasionally nausea and vomiting.

The veratrum alkaloids which have been studied in detail have been shown to produce hypotension by acting upon certain receptors whose impulses travel to the vasomotor center via the vagus and the carotid sinus nerves. Two alkaloids have been studied in sufficient detail to eliminate or implicate additional pathways of hypotensive action. One of these, protoveratrine A, has been found not to have sites of action other than those mediated through the vagus and the carotid sinus nerves, while the other, veratridine, has been shown to have activity at other sites. These additional sites may be central. None of the veratrum alkaloids have been found to have direct action on vascular beds.

HAROLD A. NASH

Cross-references: *Asymmetry, Optical Rotation, Toxicity, Toxicology*

ALKYD RESINS

Alkyd resins are the reaction products of polyhydric alcohols and resinifying polybasic acids. The term "alkyd" was coined by R. H. Kienle to indicate the origin of the resins from alcohols and acids ("acid"). These resins are important raw materials for every type of organic coating, including paints, enamels, lacquers, varnishes, and industrial and automotive finishes. They impart high gloss, good adhesion, good resistance to weathering, and long life protection at reasonable cost. Their resistance to alkalis is generally poor, but it can be improved with modifying agents.

The first alkyd resin was prepared by Berzelius in 1847 from glycerol and tartaric acid. In 1851, Van Bemmelen obtained a resin from glycerol and adipic acid. The first alkyd resins to become industrially important were glyceryl phthalate resins prepared by the polycondensation of phthalic acid or anhydride and glycerol. The glyceryl phthalate resins were introduced in 1901 by W. Smith but did not gain wide application until the development of the phthalic anhydride industry after World War I.

The alkyd resins now being produced may be divided into two major groups based on the principal acid reactant: (1) phthalic alkyd resins and (2) maleic alkyd resins. The phthalic alkyds are produced in considerably larger volume than the maleic alkyds (1953 production: phthalic alkyds, 390,527,000 pounds; maleic alkyds, 57,111,000 pounds). The phthalic alkyd resins are essentially modifications of glyceryl phthalate. The most important modifying agents include other polybasic acids and polyhydric alcohols, drying oils and the fatty acids derived from them, and natural and synthetic resins.

Maleic alkyd resins include resins prepared from maleic anhydride or acids derived from maleic

anhydride by Diels-Alder or other addition reactions. The latter type includes the glyceryl esters of adducts of maleic anhydride with rosin, abietic acid, terpenes, and conjugated diolefins such as cyclopentadiene (Carbic acid resins). The adduct resins may be modified with oils. Oil-modified straight glyceryl maleates, however, are not manufactured to a great extent because of the relatively high cost of maleic anhydride as compared to phthalic anhydride.

Alkyd resins in which neither phthalic anhydride or maleic anhydride is the principal acid reactant amount to only a small proportion of the total alkyd resin production (18,862,000 pounds in 1953). Some of the acids used include the dimer of abietic acid, sorbic acid, pelargonic acid, azelaic acid, and methylenedisalicylic acid. Isophthalic acid gives alkyds of excellent film strength.

Glycerol is the principal polyhydric alcohol used in alkyd resins. Other alcohols used alone or as modifying agents are ethylene, diethylene, and triethylene glycols, sorbitol, mannitol, and pentaerythritol. The glycols increase the flexibility of the resins. Sorbitol, mannitol, and pentaerythritol react more readily than glycerol with acid constituents. Pentaerythritol has four hydroxyl groups and thus permits a high degree of crosslinking with resultant increase in hardness.

The leading modifying agents for alkyd resins are drying oils and the fatty acids derived from them. Alkyd resins are also modified with semidrying oils and with nondrying oils. The drying and semidrying oils used include linseed, soybean, tall, tung, and dehydrated castor oils. The soybean oil alkyds have the best color retention. Cottonseed, castor, and coconut oils are the commonly used nondrying oils. The alkyd resins are distinguished by the amount of oil component they contain as well as by chemical composition. Generally, short oil alkyds contain less than 35 per cent by weight of oil, medium oil alkyds about 50 per cent of oil, and long-oil alkyds more than 60 per cent of oil.

The higher the oil content, the more flexible is the resin. Compatibility for blending with oil-based paints or vehicles also increases with oil content. Long-oil alkyds are generally blended with aliphatic solvents, but short-oil alkyds require aromatic solvents. Medium-oil alkyds are compatible with both long- and short-oil alkyds. The long-oil alkyds are used mainly in air-drying coatings such as architectural paints. The short- and medium-oil alkyds are used for both air-drying and baking finishes, although the short-oil alkyds are usually baked to give very hard, durable finishes. The semidrying oil alkyds are used in low-temperature white baking finishes, as in finishes for refrigerator and other kitchen equipment. They cannot be matched by other types of products for this purpose. They are also used in lacquers to impart adhesion and flexibility. Nondrying oil alkyds are used almost exclusively in lacquers and as plasticizers for other resins.

Maleic anhydride is the most important polybasic acid modifying agent for phthalic alkyd resins. When used alone or with ester gums, it gives very hard resins. Fumaric acid gives even

harder resins. Succinic, adipic, and sebacic acids increase flexibility.

Both natural and synthetic resins are used to modify alkyd resins. Phenolic resin-modified alkyds have improved water and alkali resistance. Baking finishes are frequently formulated with urea-formaldehyde and melamine-formaldehyde resins to increase hardness and durability. A relatively small proportion of silicone in the alkyd will materially improve high-temperature and weathering resistance. Modification with natural resins such as rosin, copals, and ester gum gives rapid drying and setting coatings with pale color and high gloss.

Alkyd resins are manufactured by direct fusion of the raw materials or by fusion in the presence of a solvent. Stainless steel or glass-lined equipment is used. A blanket of inert gas is maintained in the reactor. The reaction temperature ranges from 350 to 470°F. Short-oil resins react faster than long-oil resins and are therefore produced in the lower area of this temperature range. Addition of maleic anhydride increases the reaction rate.

The phenolic resin modified alkyds are prepared by adding a rosin-modified phenolic resin toward the end of the alkyd reaction or a condensate of formaldehyde and a phenolic compound at the beginning of the reaction.

Instead of using fatty acids in the alkyd process, it is possible to use a fatty oil together with the amount of glycerol necessary to form a fatty acid monoglyceride. The oil, glycerol, and some lime are heated, and then the acid compound is added. This "monoglyceride process" is used particularly for the long oil alkyds.

The consumption of alkyd resins of all types in United States was over 400 million pounds in 1953, as compared to only one million pounds in 1927.

Year	Production (pounds)	Sales (pounds)
1914	237,883,000	219,685,000
1946	245,371,000	206,280,000
1948	288,253,000	170,751,000
1950	401,966,000	225,256,000
1952	431,266,000	255,577,000
1953	418,945,000	226,535,000

(Source: U. S. Tariff Commission)

JOHAN BJORKSTEN

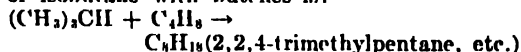
Cross-references: *Alcohols, Glycerol, Protective Coatings, Fatty Acids, Plastics, Paints, Diels Alder Reaction*

ALKYLATION

Alkylation, in broad terms, is the process by which an alkyl radical is introduced, by addition or substitution, into an organic compound. Alkylation may be classified according to the type of chemical bonding formed with the alkyl group. The process includes reactions whereby alkyl groups are bonded with carbon, nitrogen, oxygen, sulfur or metals to form compounds such as isoparaffins, alkyl amines, ethers, mercaptans, metal alkyls, etc. Commonly used alkylating agents are olefins, alkyl halides and alcohols.

In the petroleum industry alkylation generally refers to the reaction of an olefin with a paraffin, aromatic or other cyclic hydrocarbon to form a hydrocarbon equal in molecular weight to that of the combined reactants. Alkylation reactions assumed great importance in World War II in the production of high-octane isoparaffins, cumene and tetraethyllead for use in aviation gasoline as well as ethyl benzene for the production of styrene, used in the preparation of synthetic rubber and plastics.

Alkylation of paraffins, particularly isobutane, with low molecular weight olefins to form high-octane isoparaffins in the gasoline boiling range, was first described in the late 1930's. The reaction of isobutane with butenes is:



Paraffin alkylation proceeds thermally at high temperatures and pressures and at low temperatures and pressures in the presence of certain acid catalysts. A high paraffin-olefin ratio is required to prevent polymerization. The thermal reaction is carried out at about 900°F and at 3000-8000 psi. Ethylene, in contrast to its low activity in catalytic processes, is more reactive than higher molecular weight olefins. The reaction of isobutane with ethylene yields neohexane as the principal product. Under thermal operation both normal and isoparaffins are alkylated. Yields per pass range from 11 to 35 per cent.

Alkylation of isoparaffins with olefins occurs in the liquid phase at low temperatures with catalysts such as sulfuric acid, hydrogen fluoride, aluminum chloride, boron trifluoride, etc. Commercially, alkylate is produced by processes employing either sulfuric acid or hydrogen fluoride as catalysts. The development of the sulfuric acid process in 1939 followed by the hydrogen fluoride process, led to a production of about 150,000 barrels of alkylate per day at the conclusion of World War II. In 1952 alkylation capacity was approximately the same.

In the sulfuric acid process, olefins such as propylene, butenes and pentenes react with isobutane in the presence of 98 per cent acid at 30-70°F and at pressures of 100-150 psi. About 3 to 8 parts of isobutane per part of olefin are charged to prevent polymerization. Practically all the olefin reacts and the excess isobutane is recycled. Consumption of acid is 0.5 to 1.0 pound per gallon of alkylate produced.

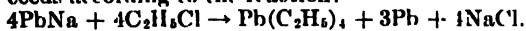
The hydrogen fluoride process is somewhat similar to the sulfuric acid operation. Temperatures of 70-115°F and pressures of 125-175 psi are employed. Consumption of acid is lower than in the sulfuric acid process thus making hydrogen fluoride competitive in spite of its higher cost.

Alkylate composition depends upon the isoparaffin-olefin ratio and upon the reactants used. Temperature, acid strength, and degree of mixing also affect composition. Isobutene is the most reactive olefin, whereas ethylene is not reacted by these acids. Aluminum chloride is used as a catalyst to produce diisopropyl from isobutane and ethylene.

In the alkylation of aromatics the production

of ethyl benzene and cumene are important industrially. Ethyl benzene results from the reaction of benzene with ethylene at 190°F over aluminum chloride as catalyst. Cumene, a component of aviation gasoline, is produced by vapor phase reaction of benzene and propylene at 400-500°F over a phosphoric acid catalyst.

Although recent emphasis has been placed upon hydrocarbon alkylation, other types of alkylation have received a great deal of attention and numerous chemicals are derived by reactions of this nature. The manufacture of tetraethyllead proceeds according to the reaction:



Consumption of this chemical, as a fuel antiknock, amounted to 530,000,000 pounds in 1952. Among the many other chemicals produced commercially by alkylation processes a few may be mentioned. Aliphatic amines result from the reaction of alkyl halides with ammonia in alcohol solution; others such as "Cellosolve" and "Carbitol", used as solvents, are products in which ethanol acts as the alkylating agent; ethyl cellulose, for plastics and protective coatings, is prepared by the action of alkyl halides on alkali cellulose. Other alkylation products include mercaptans from alcohols and hydrogen sulfide and silicon organics which show promise of application in lacquers, resins and lubricants.

H. O. FALKINS

Cross-references: *Gasoline, Antiknock Agents, Petroleum*

ALLERGY

In its immunological sense the term "allergy" means an altered degree of susceptibility caused by an inoculation and manifested in reaction to a subsequent inoculation with the same serum, as in anaphylaxis. Present concepts of allergy have developed through observations of clinical manifestations in the tissues of man and animals correlated with experiments on the serological specificity of proteins, cell antigens, the nature and the specificity of antibodies, the mechanism of sensitization by artificially conjugated antigens, the mechanisms of serological reactions of simple chemical compounds, chemical investigations on nonprotein substances reacting specifically, and the mechanisms of antigen-antibody reaction. In the attempt to relate chemistry and physics to immunology and allergy the experimenter was always confronted with the questions: (1) What molecules are involved? (2) How do these molecules react to produce antibodies and to react specifically with the antibodies thus produced?

Very well known indeed is the chemistry of small molecules and remarkably well organized is our knowledge of the way in which they produce sensitization in animals and in man. However, until about 1940, nearly all these immunologic mechanisms were restricted to small known organic molecules or of larger molecules of unknown structure. Since then there has been a new and rapid development of our knowledge not only of

small molecules but also of large naturally occurring molecules of proteins.

Electrophoretic separation has made it possible to isolate the main colorless constituents found in pollen extracts of giant ragweed, or dwarf ragweed and of timothy grass, and to characterize some of their chemical and immunologic properties as well as those of the pigmented molecules. It has been found that the molecules responsible for clinical pollen hay fever and asthma are not the large protein antigens, as had hitherto been thought. The cause of the symptoms of pollinosis has been found to be comparatively small molecules, having molecular weights not much more than 5,000, and having properties similar to but not characteristic of proteins. These molecules, which have been isolated in highly purified form, have been named as follows:

(a) In giant ragweed pollen (*Ambrosia trifida*), the main constituent has been called "Trifidin".

(b) In dwarf ragweed pollen (*Ambrosia artemisiifolia*), the main constituent has been called "Artefolin".

(c) In timothy pollen (*phleum pratense*), the main colorless constituent was named "Pratensin".

Similar results were found in the electrophoretic analysis of June grass, Bermuda grass, sheep sorrel, English plantain, birch and red oak. Electrophoretic analysis showed a general similarity of all of the patterns with main colorless constituents and minor pigmented fractions, the activity of which, based on the evidence obtained thus far, indicates biological activity in both the pigmented molecules and the pigment free colorless components.

To determine the approximate size of the molecules, the rate at which they sedimented in the ultracentrifuge was ascertained. They do so much more slowly than serum albumin. By correlating the ultracentrifugal data with diffusion studies, it was found that these molecules had molecular weights of about 5,000 each—rather low for the molecular weight of a typical protein. It appears that these molecules are closer to high molecular weight polypeptides, are more diffusible than proteins, can permeate the living system more readily, and show greater stability in the presence of heat.

The reactions of Trifidin and Artefolin with serum diluted 1:30 indicate that they are high-molecular-weight polypeptides, coupled with other molecules formed more or less like carbohydrate molecules, and that much more careful chemical work will be required on these fractions to determine their precise chemical nature. This type of experimentation will lead to the explicit evaluation of a chemical structure of pollen antigen molecules.

Whereas two decades ago there were most complicated theories regarding the nature of proteins, the ultracentrifugal study of electrophoretically purified proteins now reveals a group of homogeneous molecules of great importance to the allergist. The type of molecule found in many pollen extracts belongs to a new class of allergens which may be called "protoproteins". The prefix "proto"

in chemistry denotes the first or the lowest of a series. A protoprotein, then, would be a substance on the borderline between the higher molecular weight polypeptides and the low molecular weight proteins. The designation of these highly allergenic molecules by the term "protoprotein" not only gives them a new name but lends to this group of molecules a new element of predictability, which enables us to state that such small molecules can diffuse more readily, can permeate living mucous membranes with greater facility and offer greater hope of synthesis in the laboratory.

HAROLD A. ABRAMSON

Cross-references: *Antibodies, Electrophoresis, Proteins*

ALLOTROPES

Allotropes are two or more forms of the same element that differ in physical properties. The cause of the difference may be in the number of atoms per molecule, as with oxygen and ozone, or in the crystal form of the element, as with diamond and graphite (also called polymorphism).

Oxygen and Ozone. The density of oxygen is 1.429 g per liter at STP; the density of ozone is 2.144 g per liter. The ratio of the densities is obviously 2/3. If we make the generally accepted deduction that oxygen has two atoms per molecule (O_2), then ozone has three atoms per molecule (O_3). The evidence for the existence of ozone (O_3) is doubtful, although O_4 molecules may exist in liquid oxygen.

Carbon. Graphite and diamond are clear-cut allotropic forms of carbon. The so-called amorphous form of carbon is apparently composed of fragments of graphitic carbon, finely divided. Evidence for this view is obtained by x-ray investigation.

Graphite is composed of slippery flakes. The product is relatively pure when prepared by electric furnace methods. Its density is 2.25 g per ml. The explanation of the lubricating qualities of graphite comes from the description of its crystalline nature. In graphite, the carbon atoms exist in sheets. The force between the adjacent sheets is small, and that between adjacent carbon atoms is much greater. Graphite is a good conductor of electricity, and is relatively soft.

Diamonds are natural crystals that are cubical, often colorless, or almost so, but sometimes found colored. They are the hardest substance known, and this property is directly related to their crystal structure. Each carbon atom in a diamond crystal "rests" on a tripod of three other carbon atoms. The three carbon atoms in the base of the tripod are in turn supported by three more, these in turn by three others, and so on. Carbon atoms in a diamond are 1.54 Å apart. The covalent bonds between adjacent carbon atoms are exceedingly stable. Diamonds have a density of 3.51 g per ml, and a relatively high refractive index, 2.1173.

Phosphorus. When phosphorus vapor is condensed, cubic crystals of white or yellow phosphorus form. They melt at 44.1°C and boil at

280°C. Their density is 1.82 g per ml. White phosphorus ignites spontaneously at about 34°C. If the pressure is as high as 12,000 atm, a hexagonal instead of a cubic form appears. White phosphorus is insoluble in water, but is soluble in CS_2 . In solution and as a vapor, this allotrope has a formula that corresponds to P_4 . It is extremely toxic, and should never be handled with the fingers. Violet phosphorus, also called α -metallic phosphorus (melting point 590°C, density 2.34 g per ml), is made by cooling a mixture of melted phosphorus and lead and then removing the lead with nitric acid. It is insoluble in most solvents, and it can be purified by sublimation at an extremely low pressure. The red phosphorus commonly used in commerce, which forms on the outside of a stick of white phosphorus exposed to light, probably consists of finely divided violet phosphorus. The red form is made by heating the yellow form under controlled conditions.

Black phosphorus, also called β -metallic phosphorus, is made by heating white phosphorus to 220°C at 12,000 atm pressure. This form conducts electricity well, weighs 2.70 g per ml, and changes to red phosphorus at 550°C.

A sooty flake form of phosphorus has been made from white phosphorus at 300°C and 8000 atm pressure. This allotrope may be amorphous. Its density is 2.25 g per ml.

Arsenic. The allotropes of arsenic, are similar to those of phosphorus. The α yellow form, As_4 , is similar to white phosphorus, but it is extremely metastable. It can be made by cooling arsenic vapor with liquid air. In the presence of light for a very short time, the more stable allotrope forms. Yellow arsenic has density about 2 g per ml, is a poor conductor of electricity, and is soluble in CS_2 . The ordinary γ form of arsenic is metallic, is insoluble in CS_2 , and is a fair conductor of electricity. Its density is 5.7 g per ml.

Sulfur. Rhombic sulfur (diamond-shaped crystals) is stable at room temperature. It consists of a staggered ring of eight sulfur atoms, four in one plane and four in another, alternately, with angles of 105° between them.

At 95.5°C, rhombic sulfur changes slowly to needle like crystals of monoclinic sulfur. It is stable from 95.5°C up to 118.7°C, its melting point. When liquid sulfur is cooled, monoclinic crystals form first. While they keep their external shape of monoclinic, at temperatures below 95.5°C they are composed of tiny rhombs, and they are very brittle.

When sulfur is melted, it becomes highly viscous at about 180°C, dark if impure, but colorless if extremely pure. Further heating causes the viscosity to decrease until sulfur boils at 444.6°C. If sulfur at a temperature slightly below its boiling point is chilled, as it is when it is poured into cold water, provided an impurity such as sulfur dioxide is present, the form called plastic sulfur is made. This form consists of a tangled brush-pile like mass of sulfur chains.

When plastic sulfur cools to room temperature, it becomes hard again. If such a mass of sulfur is extracted with CS_2 , the rhombic sulfur in it can

be removed. The remaining allotropic form of sulfur, insoluble in CS_2 , is amorphous sulfur, or S_μ .

Selenium. The so-called amorphous forms of selenium (1) bright red when precipitated, or (2) vitreous when liquid selenium is cooled rapidly, are probably not definite allotropic forms.

Selenium is known to exist as Se_8 in solution, as Se_2 in vapor form, and as monatomic molecules at a higher temperature of the vapor. In crystalline form, evidence exists for the interpretation that selenium atoms form strings of spiral chains of selenium atoms.

Tin. The familiar metallic form of tin (β) is an allotrope stable above 13.2°C . Such tin melts at 231.8°C as do all forms of tin, and it has a tetrahedral crystalline structure in which adjacent tin atoms are more than 3 \AA apart. Below 13.2°C , tin changes slowly to a gray powdery form (α) which has a cubical structure, and in which the interatomic space is 2.8 \AA . The transition is most rapid at -50°C . A third allotropic form of tin (γ) is a rhombic brittle form that comes when liquid tin solidifies slowly. It is stable above 161°C .

Iron. The form of iron that is stable at the lowest temperature up to 912°C is α (ferrite, body-centered cubic). It is magnetic up to 750°C . Gamma (γ)-(austenite, face-centered cubic) is a nonmagnetic isotope, and it is stable above 912°C . Delta (δ)-ferrite (body-centered cubic) is possible between 1400°C and the melting point of iron, 1535°C .

Other Elements. The following elements are reported to have two or more polymorphic crystalline forms: Be, Ca, Ce, Cr, Co, Hf, La, Mn, Np, Ni, O, Pr, Rh, Ru, Sc, Sr, Ta, Ti, W, U, Zr.

ELBERT C. WEAVER

Cross-references: *Elements, Crystallography*

ALLOYS

Alloys are metallic substances containing more than one metal or in certain instances a metal and one or more nonmetals. From a constitutional viewpoint we may divide alloys into broad groups: (1) the constituents are only partly miscible in the liquid state; (2) the constituents are miscible in the liquid state but separate into two or more phases on solidifying; (3) the constituents are miscible in both liquid and solid states at least over a considerable composition and temperature range. The third group is by far the most important because the solid solutions and their decomposition products provide the greatest variation in properties.

Alloys may be classified on such a constitutional basis, but in an article of limited scope it is preferable to consider them according to their basis metal, indicating in each case the constitutional basis for the special properties which make the alloy important.

Iron-Base Alloys. Iron alloys, which include steels, are by far the most important from the standpoint of volume production and diversity of properties. The steels are basically iron-carbon alloys, and depend for their properties on the fact that carbon forms a solid solution with the high-

temperature gamma form of iron, while it does not dissolve in the low-temperature alpha form, separating eventually as iron carbide. The properties of the steel depend on the manner in which the iron carbide is separated.

When plain carbon steel is quenched it becomes hard due to the formation of martensite, a transition phase between the gamma solid solution and the alpha form. When this very hard steel is tempered by heating to relatively low temperatures, iron carbide separates in more or less coarse particles, which determine the hardness. The addition of other metals to iron-carbon alloys produce alloy steels. Tungsten and molybdenum act to prevent the tempering or softening of steels on tempering even at a red heat. Such steels are called high-speed steels because they do not soften from heating by high speed cutting. Chromium brings about rustless characteristics. Stainless steels are produced by adding nickel and chromium to low-carbon steels.

Other iron alloys are used because of the unique magnetic property of iron. Silicon iron alloys are used for transformer cores because of their magnetic softness, while iron alloys with several metals, particularly cobalt, nickel, and aluminum, are used for permanent magnets. All alloys in which the iron is in the low temperature or alpha form are magnetic. Structurally these alloys have high permeability and low coercive force if they have large magnetic domains in which the atomic arrangement is uninterrupted. Conversely, when the alloy is broken up into submicroscopic domains by fine precipitates or superstructures they have high coercive force. The magnetically useful iron alloys are accordingly either solid solutions or their decomposition products. Cobalt, when alloyed with iron, has the unique property of increasing the field at which the alloy becomes magnetically saturated.

Another group of iron alloys, also solid solutions, are the iron-nickel alloys containing 40-50 per cent nickel. These alloys have very low coefficient of thermal expansion and include the alloy known as "Invar", which has almost zero coefficient at room temperature.

Copper-Base Alloys. From a volume standpoint, copper alloys, including brasses and bronzes, rank second to iron alloys. The brasses are copper-zinc alloys varying from 55-70 per cent copper. The higher copper alloys are more ductile, and the 70 per cent alloy is known as cartridge brass because it permits the deep drawing necessary for cartridge cases. The lower copper brasses are familiar in many uses. When the copper content falls below 63 per cent, the alloys contain another solid solution known as beta, which is characteristically hot workable even when up to 1.5 per cent lead is added, to increase the ease of machining. All the brasses are solid solutions. Bronzes are alloys of tin and copper, but due to the scarcity of tin, are not so widely used as they once were. Several commercial copper alloys are commonly referred to as bronze even though they contain only small amounts of tin. Manganese bronze is a copper alloy containing manganese, tin and iron which is used for ship propellers.

Beryllium bronze is an alloy of copper and beryllium which, like steel, can be heat treated to provide a wide range of properties. An alloy having similar hardening properties is composed of copper with 20 per cent manganese and 20 per cent nickel. These alloys are solid solutions in various degrees of decomposition. Phosphor bronze is a term used to describe copper alloys containing 1-10 per cent tin and a trace of phosphorus. Another group of copper alloys consists of copper nickel-zinc, and is known as nickel silver. These may contain 18-30 per cent nickel. These alloys, which are solid solutions, are strong, corrosion-resistant, and silver colored. They are used for many purposes, but particularly for tableware which is silver plated.

Aluminum-Base Alloys. Many aluminum alloys are widely used. Aluminum silicon alloys containing 12 per cent silicon are used for castings. The crystallization of these alloys can be greatly changed by adding a little sodium called "modification". Wrought alloys of aluminum contain either about 4 per cent copper and 0.6 per cent magnesium or about 1 per cent silicon and 1 per cent magnesium. These alloys are related to "Duralumin", one of the first "age hardenable" alloys discovered by Wilm in 1911. The study of this alloy resulted in an important contribution to our knowledge of controlling alloy properties by decomposition of solid solutions by heat treatment.

Nickel-Base Alloys. The most important of the nickel base alloys is monel metal, a nickel copper solid solution containing about 70 per cent nickel. The alloy was originally produced by combination smelting of nickel and copper ores. It is widely used for its corrosion resistant properties. Several nickel alloys of the dispersion hardening type have been developed such as K monel, which contains copper and aluminum. A very important alloy of nickel is the nickel chromium alloy containing about 20 per cent chromium. This alloy has high electrical resistance, and great resistance to oxidation at high temperatures. It is accordingly used for electrical heating elements. Several nickel base alloys are useful for magnetic purposes. An alloy of 78.5 per cent nickel, balance iron, has very high permeability at low fields. It is called "Perm alloy" and has been used for the continuous inductive loading of transatlantic cables. The alloy of 50 per cent nickel, 50 per cent iron has very high permeability at higher fields such as those in transformers.

Lead and Tin Alloys. The most familiar of lead-tin alloys is solder, which usually contains 40-50 per cent tin. It is used for its low melting point, and ability to wet metals which are to be joined. The solders are alloys in which the two metals are miscible in all proportions when liquid, but which separate into two solid phases as they solidify. This fact is of importance in the properties of solders because in alloy systems of this type there is a large temperature interval between the point at which freezing begins and the point at which it ends. This range is called the plastic range, since in it the alloy is partially solid and

can be formed into the desired shape. This forming is known as "wiping" in soldering procedures.

Lead and copper are immiscible in both liquid and solid state. By the addition of a third material, such as sulfur, the liquid metals can be emulsified and after solidification find use as bearing metals, since they are composed of relatively hard copper globules in soft lead. Lead alloyed with about 3 per cent tin is used for cable sheath, although this has been largely replaced with 1 per cent antimony. Storage battery plates are made from "hard lead" an alloy of lead with 10-13 per cent antimony.

Tin base alloys are also important as bearing metals, commonly known as babbit metal. These alloys contain 83-91 per cent tin, 4.5-8.5 per cent antimony, and 3.5-8.5 per cent copper. The value of these alloys as bearing metals depends on their structure which consists of hard crystals of tin-antimony compound in a softer matrix. Type metals are lead base alloys containing 11-25 per cent antimony, and 3-13 per cent tin. Modern pewter is a tin base alloy containing 4-6.5 per cent antimony, 1-1.5 per cent copper.

Manganese-Base Alloys. Two alloys with manganese base are of importance for their special properties. A manganese copper-nickel alloy has unusually high coefficient of thermal expansion, while manganese copper alloys containing about 20 per cent copper have a very high vibration damping capacity. This high damping capacity is accompanied by an abnormally low shear modulus, giving the alloy a high degree of surface conformance desirable for cams and other friction drives.

Magnesium-Base Alloys. Several magnesium alloys are used in the form of castings and extrusions because of the low specific gravity of these alloys. Most of the magnesium alloys contain 3-6 per cent aluminum, 1-5 per cent zinc, and 0.2-1.5 per cent manganese.

Precious Metal Alloys. The most important and familiar precious metal alloy is sterling silver—an alloy of silver and copper containing 92.5 per cent silver. Coin silver contains from 50-90 per cent silver, balance copper. United States coins contain 90 per cent silver. The silver is alloyed to increase its hardness and strength. Silver solders are alloys of silver, copper, and zinc which are much stronger than lead-tin solder.

Gold alloys are less common than silver, but are widely used for jewelry. Ordinary or yellow gold is an alloy of gold with copper or copper and silver. The amount of gold in the alloy is expressed in parts in twenty-four, called "carats". 14 carat gold is 14/24 or 58.33 per cent gold. White gold is usually a complex alloy the basis of which is gold-nickel.

Platinum alloys are usually those with other platinum group metals, such as iridium and ruthenium which harden platinum. These alloys are used for scientific purposes and for fine jewelry.

Titanium Alloys. Titanium alloys have recently achieved considerable importance because of their combination of light weight and great strength. The most important alloys contain 8 per cent manganese; 4 per cent aluminum, 4 per

cent manganese; and 5 per cent aluminum, 3 per cent chromium.

Cobalt-Base Alloys. Cobalt-base alloys have become important because of their high temperature hardness and oxidation resistance. Such alloys are used in jet engines and rockets and have been called "superalloys". The cobalt is alloyed with chromium and with one or more of the elements nickel, molybdenum, tungsten and columbium.

Zinc Alloys. Zinc is more important as a minor alloying element than in zinc-base alloys; however, a number of zinc alloys are used for die castings which find use in inexpensive hardware. Zinc die-casting alloys contain copper, aluminum and magnesium.

While not used as such, the alloy system lead zinc is of considerable commercial importance. It has limited liquid miscibility. In such a two-liquid layer system silver and gold are concentrated in the zinc layer and are removed by solidifying the zinc crust. This process, known as the Parkes process, is used for removing silver and gold from crude lead.

Bismuth and Cadmium Alloys. Bismuth and cadmium are used as alloying elements in the fusible alloys sometimes referred to as Wood's metal. An alloy of 50 per cent bismuth, 27 per cent lead, 13 per cent tin, and 10 per cent cadmium melts at 70°C. Alloys with other proportions of these metals melt up to 144°C, and by the addition of indium the melting point can be lowered to 47°C.

R. S. DEAN

Cross-references: *Metals, Metallurgy*

ALPHA PARTICLES

Alpha particles, sometimes called rays, are spontaneously ejected from the nuclei of many radioactive elements as doubly charged helium nuclei with extremely high velocity ($\frac{1}{15}$ to $\frac{1}{20}$ that of light). Until recently the radioactive alpha particle represented the highest concentration of kinetic energy known to science. But with the advent of the cyclotron of Lawrence, helium (and other light nuclei) could be raised to much higher energies limited only by the cyclotron voltage, thus generating so-called artificial alpha particles, which are used to bombard nuclei to produce other isotopes and to study their effects in radiation chemistry.

All alpha particles have the same mass as the helium atom (4) and the same charge of 2 units representing the loss of two orbital electrons giving the stripped nucleus He^{+2} . (For a list of alpha radiators see the Table under Radium).

An alpha particle travels in straight line through the electronic field of a large number of atoms or molecules (150-200 thousand in air) and only rarely suffers a large deflection by close collision with a nucleus. The kinetic energy is spent in collision by producing ionization (removal of one or more electrons), by excitation, and in other minor ways. In the five noble gases when highly pure, Jesse has found that the proportion of total energy expended

by the alpha particle to the energy used in producing ionization is constant, having the value 1.73, or that 36.6 per cent is spent in ionization and 63.4 per cent in excitation, etc. The proportion of energy spent by alpha particles in exciting gas molecules (principally organic molecules in contrast to atomic gases) is somewhat higher and variable (67 per cent for butane, 73 per cent for oxygen).

When an alpha particle impinges on certain solid materials, especially phosphorescent zinc sulfide, a scintillation is produced which can be observed under suitable magnification. By counting the number of scintillations per unit time from a known quantity of radioactive material much valuable information is obtained about the properties of alpha particles and their interaction with matter. Historically this was of the highest importance. Later other types of counting by electrical discharge (Geiger counters) were introduced. More recently scintillation counting, especially for gamma rays, has again been successfully adapted by the use of photomultipliers. Luminous paints, such as are used on watch and clock dials, are made by mixing radium (or mesothorium) sulfate with phosphorescent zinc sulfide. The large number of scintillations gives a continuous luminescence visible to the rested eye.

If alpha particles pass through a chamber containing a gas saturated with water vapor they produce ionization along their paths. If the gas is suddenly expanded so as to produce supersaturation, condensation of water droplets occurs on the ions before they can diffuse. With suitable illumination the Wilson cloud tracks can be observed or photographed. Path length and form, including pictures of nuclear collisions and energy distribution among the fragments, are thus disclosed.

Owing to their high energy and ease of absorption by gases, alpha particles have been used as activating agent for many chemical reactions. Radon mixed with the gas or mixture of gases is a suitable system for chemical kinetic studies.

S. C. LIND

Cross-references: *Protons, Electrons, Radioactivity, Radium*

ALUMINUM AND ITS COMPOUNDS

Aluminum is a trivalent metal occurring in Group III of the Periodic Table. It has a molecular weight of 26.97 and atomic number of 13. It is in the fourth position of the Electromotive Series of metals.

Production. Although aluminum is the world's most abundant metallic element, comprising some 8 per cent of the earth's crust to a depth of about ten miles, it is now produced commercially only from bauxite. Large deposits of bauxite occur in many parts of the world, but mostly in tropical and subtropical areas.

High-grade bauxite contains from 50 to 60 per cent aluminum oxide, or alumina, chemically combined with 12 to 32 per cent water to form a hydrated oxide. The ore also contains silica (silicon oxide) 2-7 per cent; iron oxide 2-20 per cent; and

titanium oxide 2-4 per cent. Traces of a number of other minerals usually are present. Bauxites of lower grade, containing from 15 to 50 per cent alumina and correspondingly higher percentages of the other oxides, are being successfully processed today.

Unlike some of the other common metals, aluminum cannot be produced directly from its ore because the metals present as impurities would be carried through the processing and become alloyed with the aluminum. For this reason the ore must first be refined to exclude the impurities. This refining operation produces alumina of high purity, from which metallic aluminum of better than 99 per cent purity is obtained.

In refining bauxite, the first operation is to mix pulverized ore with appropriate amounts of soda ash, crushed lime and water, which form a solution of caustic soda. This mixture is pumped into large digesting tanks into which steam is admitted under pressure. Motor driven agitators bring all the materials into intimate contact. In the digesters, the alumina content of the bauxite is converted into sodium aluminate, which is soluble. The unwanted materials, which are insoluble, are separated by subsequent settling and filtering. The filtered sodium aluminate solution then is pumped through cooling towers and precipitators, and hydrated alumina is recovered as a solid. The hydrated alumina thus obtained is passed through rotary kilns at a temperature of about 1800°F to drive off the chemically combined water, emerging white hot as virtually pure alumina at the discharge end. After cooling, the alumina is ready for shipment to reduction plants.

The solid residues removed by settling and filtering contain not only the unwanted silica and other oxides but also an amount of alumina and soda equivalent to their silica content. Only ores of low silica content thus can be processed economically in this manner. For ores containing higher proportions of silica, the so-called "combination process" is used. With this process, the filtered residues are sintered with soda ash and limestone. The resulting sinter is leached with water containing a little caustic soda to produce a solution of sodium aluminate with only a small amount of silica. This solution is returned to the digesters for reprocessing.

Separating the metal from its oxide (reduction) is accomplished electrolytically by passing an electric current through a solution of alumina in molten cryolite in large carbon lined steel cells or "pots". The electrolyte is maintained in a molten state by the heating effect of the electric current, and certain fluorides are added to facilitate the action. Molten aluminum is deposited on the bottoms of the pots. At regular intervals it is siphoned out into large ladles, from which it is poured into pig or ingot molds.

Properties. As it comes from the electrolytic pots, aluminum has a purity of 99.0 per cent or higher. The impurities are mostly silicon and iron, with smaller amounts of titanium. Where a metal of higher purity is required, further refining is necessary. Methods now in commercial use will produce aluminum up to a purity of 99.99 per cent.

Aluminum is available in practically all forms—plate, sheet, foil, rod, bar and wire, rolled structural sections and other rolled shapes, extruded sections, tube and pipe, castings of all types, powder and paste. It can readily be formed or shaped by practically all metal-working processes. It can be welded, brazed and soldered. It is commonly alloyed with small percentages of other metals to give it increased strength and hardness, improved casting characteristics or other desired properties. Both the metal and its alloys are strengthened and hardened by mechanical working, such as cold-rolling, and some of the alloys are further strengthened by heat treatment.

Like other metals, aluminum and its alloys lose part of their strength at elevated temperatures, although some alloys retain good strength at temperatures up to 400-500°F. At subzero temperatures, however, their strength increases without loss of ductility, making aluminum a particularly useful metal for low-temperature applications.

When aluminum surfaces are exposed to the atmosphere, a thin invisible oxide skin forms immediately which protects the metal from further oxidation. This self-protecting characteristic gives aluminum its high resistance to corrosion. Unless exposed to some substance or condition which destroys this oxide coating, the metal remains fully protected. Aluminum thus is highly resistant to weathering, even in industrial atmospheres which often corrode other metals.

Many acids have little corrosive effect on aluminum. In many cases, the rate of attack depends partly on the concentration of the acid or on other factors relating to service conditions. For example, fuming nitric acid and glacial acetic acid have little effect on aluminum, but dilute solutions of these acids attack the metal slightly, particularly if hot. In certain concentration ranges sulfuric acid also may cause corrosion, but the metal has been used successfully in contact with solutions containing as much as 5% sulfuric acid. Aluminum with anodically applied oxide coatings has been successfully used with sulfuric acid in strengths up to 15% solutions. Simple organic acids such as acetic, citric, lactic and tartaric, and fatty acids have virtually no action on aluminum at room temperature. The presence of a small amount of water (even as little as a few tenths of one per cent) is sufficient to prevent action by fatty acids at elevated temperatures. Most of the fruit acids likewise do not attack the metal, and the addition of sugar acts as a corrosion inhibitor.

Alkali metal hydroxides and alkaline earth hydroxides attack the oxide skin and therefore are corrosive to aluminum. Nevertheless, certain mild alkalies can be rendered compatible with the aid of inhibitors. Ammonia and amines are used successfully with aluminum.

Some alloys are less resistant to corrosion than others. These alloys often are protected from corrosive influences by cladding their exposed surfaces with a thin layer of either pure aluminum or one of the more highly corrosion-resistant alloys. The resulting Alclad alloys, as they are called, are composed of a core selected for the desired physical properties and a cladding that will

afford electrochemical protection to the core. This family of materials is especially suited to service in environments where avoidance of perforation is paramount, as in roofing and heat exchanger tubes.

A word of caution should be mentioned in connection with the corrosion-resistant characteristics of aluminum. Direct contacts with certain other metals should be avoided in the presence of an electrolyte; otherwise galvanic corrosion of the aluminum may take place in the vicinity of the contact area. It is good practice to select alloys having similar solution potentials in the expected electrolyte to avoid galvanic action.

Uses of Aluminum Compounds. A number of aluminum compounds have important chemical applications. Although a high percentage of all the alumina produced is utilized for aluminum production, this compound also has many other uses. One of the most important of these is in abrasives. Some of the most efficient abrasive materials contain alumina as either the sole or an essential ingredient. Substantial quantities of alumina are used in quick-hardening cements. This compound also is an important constituent of certain ceramic products including some types of glass, vitreous enamel, pottery and china glazes, refractory bricks and spark plug insulators. Both bauxite and alumina are used to produce aluminum sulfate for water purification purposes. Pure alumina in hydrated form is used for the production of high grade iron-free alum. Hydrated alumina also is used in the production of aluminum nitrate, aluminum chloride, aluminum phosphate, aluminum fluoride and zeolite. Other uses of hydrated alumina are as a pigment for paper-coating mixtures and in rubber compounds. A relatively new application is as a filler in some types of plastic products where alumina improves abrasion resistance and increases the hardness of finished plastic pieces.

Activated alumina, a highly porous form of the compound which is highly adsorptive, is an efficient desiccant for both gases and vapors as well as liquids. It is widely used by the petroleum industry for the removal of moisture from both vapors and liquids and from natural gas. This industry also uses a number of aluminum compounds as catalysts in its refining processes.

Aluminum fluoride is one of the compounds that is important in the production of metallic aluminum, along with cryolite, which is a double fluoride of sodium and aluminum. The latter compound also is used in ceramics and as an insecticide. Some cryolite is imported from the largest known natural deposit in Greenland, but much of it is manufactured from fluorspar, a fluoride-bearing mineral, and alumina.

THE ALUMINUM ASSOCIATION

Cross-references: *Alloys, Corrosion*

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

Founded in 1848, the Association has as its objects "to further the work of scientists, to facili-

tate cooperation among them, to improve the effectiveness of science in the promotion of human welfare, and to increase public understanding and appreciation of the importance and promise of the methods of science in human progress." It was the first and still is the only American scientific society national in scope, with interests extending into all the fields of the natural and social sciences, and open to all scientists.

For the first third of its history, the Association served as the focal point for the special fields of science. As science grew, the need for more specialized societies and meetings became imperative and many of the large thriving scientific organizations of today grew out of the sections of the Association and then became affiliates of the parent group. There are now 265 societies and academies affiliated or associated with the AAAS, and individual membership has grown to over 50,000.

The first meeting in September, 1848, was organized around two sections: "Natural History, Geology, etc." and "General Physics, etc." These two sections have evolved by a process of subdivision into 18 sections, each with an appointed secretary who serves for four years and an annually elected chairman who also holds the title of vice-president of the Association. The program of the section is developed by a section committee composed of the Council representatives of the societies affiliated with that section, the secretary and vice president of the section, plus four members-at-large. The Council as a whole elects the Board of Directors and officers and determines general policy.

Chemistry first appeared as a specific part of the program at the 1850 meeting in New Haven. The Section of Chemistry and Mineralogy scheduled five sessions with 29 chemical papers. At the Hartford, Connecticut, meeting in 1871 a request from the previous year calling for a subsection on chemistry under Section A was approved, and S. W. Johnson served as the first chairman. The Cincinnati meeting in 1881 marked the establishment of the full-fledged section on chemistry, Section C.

Although the American Chemical Society (founded in 1876) did not actually spring from Section C, the Section Committee spearheaded by F. W. Clarke and H. W. Wiley played a key role in putting the floundering young society on a firm national foundation. Although the ACS has long since outgrown the possibility of holding joint meetings with the AAAS, both the Section C Committee and the Association have enjoyed continuous close cooperation with both the local sections and the national office of the American Chemical Society, not only in the conducting of meetings but in many other efforts toward the advancement of chemistry and science as a whole. Two important examples are the AAAS Cooperative Committee on the Teaching of Science and Mathematics with members from the ACS and its Division of Chemical Education and the joint sponsorship (along with other groups) by the Society and Association of the Scientific Manpower Commission.

Publications. The publications of the Association have always played an important role in the dissemination of chemical knowledge. In the early years, before the meetings became so large as to make it impossible, the publication of the "Proceedings" supplied an annual review of significant advances in chemistry as well as other fields.

From the time of its establishment by Thomas A. Edison in 1880, *Science* has published a continuous account of important technical developments. It has been an official journal of the AAAS since 1900 and brings to scientists over the world every week news of scientists and science and technical papers reporting the results of current research.

The Scientific Monthly, the other official magazine of the Association, offers a wide variety of semitechnical articles in both the natural and social sciences designed to inform both specialist and layman of new and interesting discoveries, observations, and the results of analytical and critical thinking.

The Association has published some 40 symposium volumes, most of them based on papers presented at its meetings. From the seventh volume (1939) on "E. C. M. Advances in Surface Chemistry and Chemical Physics" to the thirty sixth (1954) on "Monomolecular Layers," chemistry has had a prominent place.

Gordon Research Conferences. The Gordon Research Conferences now represent the Association's most important activity in chemistry. Dr. Neil E. Gordon organized the first summer conference of the series at Johns Hopkins University in 1931. From this small meeting of 25 faculty members and students of the University, the movement has grown to a total of 32 conferences with an attendance of over 3000 participants from around the world. Far more important than numbers has been the increasingly significant stimulus to chemical research afforded by these informal week-long meetings.

After four years on the Hopkins campus, the conferences were moved to Gibson Island, Maryland, on Chesapeake Bay, a spot more conducive to leisurely informality and recreation than a city university could provide. By 1947 the facilities at Gibson Island could no longer accommodate the conferences, and they were moved to Colby Junior College, New London, New Hampshire. Subsequent expansion has required the establishment of two additional centers at New Hampton School, New Hampton, N. H., and Kimball Union Academy, Meriden, N. H.

Each conference is a continuing autonomous entity on a specialized but fairly general subject, e.g., polymers, catalysis. The group attending one year selects the special phase of the subject to be covered the next year and elects a chairman to arrange the program (unless a previously elected vice chairman becomes chairman). The chairman, with the assistance of the Director of the GRC, selects those privileged to attend, a maximum of 100, from the applicants. Those selected must be active mature researchers who can contribute both information and ideas. Every effort is made to distribute attendance from among academic, governmental, industrial, and foreign

laboratories. Funds are available to assist foreigners and academic scientists.

JOHN A. BEHNKE

AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS

Formed "to promote increase of knowledge of the application of dyes and chemicals in the textile industry, to encourage in any practical way research work on chemical processes and materials of importance to the textile industry, and to establish for its members channels by which interchange of professional knowledge among them may be increased", the Association was organized in Boston on November 3, 1921. In accordance with a resolution taken at a meeting during the week of the Chemical Show in New York the previous August, the inaugural meeting of the AATCC was held at the Engineers Club in Boston. About 300 invitations to become charter members of this new body had been sent out to a representative list of textile chemists associated with textile or dyestuff manufacturing industry, or interested in dyestuff application. Formation of local sections of the AATCC followed closely upon the inaugural organization. At present there are nine local sections operating under the direction of the Officers of the Association. Membership in the AATCC has grown from 1000 in 1930 to over 7000 in 1953. Corporate membership is also permitted and encouraged.

Meetings of the members of all the local sections are held annually, at which time technical discussions are held, papers presented and outstanding speakers are heard. A feature of these conventions is an Intersectional Contest in which the various sections vie for honors with original research studies. The Association also has a placement service for its members.

Probably the most important facet of the AATCC is its program of standardization of test procedures. A national Research Committee appoints permanent committees to investigate and make reports on various methods of testing the properties of fibers and dyes, such as light fastness, wash fastness, dimensional stability, flammability, chlorine retention, and for evaluation of detergents, moth proofing agents, durable finishes, and the like. From the reports of these committees, standard methods of testing and evaluation are set up.

The AATCC is closely associated with the Textile Research Council. These two organizations founded the U.S. Institute for Textile Research in 1930. In 1944 an agreement was reached with the Textile Research Institute to avoid any duplication of effort by mutual discussion of new projects. The Textile Research Institute proposes to undertake fundamental and applied research. The AATCC would be concerned primarily with wet-processing of textiles and would be preeminent in the development of standard test methods for the use of the dyer, colorist, finisher, textile chemist, converter and consumer.

At the present time the AATCC is working

jointly with the Society of Dyers and Colourists in England on the publication of a new "Colour Index," which will describe the chemical structure and method of manufacture and application of all synthetic dyestuffs.

The Association sponsors Student Chapters in connection with textile schools or similar educational institutions.

The official organ for publication of proceedings and technical papers is the *American Dyestuff Reporter*, published by Howes Publishing Co. in New York. Besides this bimonthly technical magazine, each member is privileged to receive each year the "Technical Manual and Year Book," which describes all standard testing procedure, and lists all proprietary products appropriate for the textile industry, with their chemical composition.

HERMAN P. BAUMANN

AMERICAN CANCER SOCIETY

The American Cancer Society is a voluntary association of people united in a common determination to control and eventually conquer cancer. Pioneer organization in this field in the United States, it is the only voluntary national health agency engaged in a comprehensive program of cancer research, education, and service. Its chief work is saving lives, relieving pain and suffering, and raising funds for research. More than 1,000,000 volunteers across the country give time and energy to aid that work. It had its beginning in 1913, when a small group of doctors and laymen met in New York City to establish a society for study and prevention of cancer, and to educate the public in the necessity for treatment at the earliest sign of malignant growth. About \$10,000 for this was raised in the first year, a pamphlet, "Facts About Cancer," was published, and discussion meetings with women's clubs were held in various cities.

Originally the organization's name was the American Society for the Control of Cancer. By 1930 its activities had been widened to include education for general practitioners. It prompted the American College of Surgeons to set up standards and plans for cancer clinics and diagnostic facilities. And in 1938 it helped inspire an Act of Congress designating April as Cancer Control Month. The Society was reorganized in 1945, when its name was changed to the present form. It greatly expanded its board of directors, to include equal numbers of doctors and laymen, and then put on its first nation-wide drive for funds.

Some of the research results are: (1) human cancer can be cultured in test tubes and in experimental animals; (2) important knowledge of chemical requirements for life of human cancer has been acquired; (3) based on this, means for relatively selective injury to or destruction of some human cancers have been contrived, though they are not cures; (4) transplantable cancers of several types in animals can be cured today to a substantial degree; (5) cancer cells develop resistance to chemical agents, originally injurious to such cells, exactly as bacterial cells do; (6) resistant cells,

however, may be injured by a second or third chemical.

Since 1945 the American Cancer Society has devoted nearly \$35,000,000 to research, allocating \$5,242,167 for this in 1951. Twenty-five per cent of all funds it raises are set aside for research. Grants-in-aid of \$150,845 went for research specifically in chemotherapy in 1953. Part of the institutional grant program also was given over to chemotherapy.

The Society is dedicated to a strictly practical objective: conquering human cancer, so its ultimate research interest lies in studies concerned directly with cancer in man. Basic research has developed chemicals already found useful in cancer therapy, alleviating pain and prolonging lives in some types of that disease. But so far there are no chemical cures.

All whose researches are supported by the Society are concentrating on well-defined zones of investigation. Chemicals which offer the most likely starting points for further experiment are: (1) hormones ACTH, cortisone, estrogens, and androgens; (2) folic acid antagonists, such as aminopterin; (3) nitrogen mustards and related compounds—triethylenemelamine, triethylene phosphoramide, 1,1-dimethanesulfonylbutane; (4) antimetabolites (mercaptopurine); (5) amino acid derivatives, for instance azaserine; (6) urethane, the only known active member of its class.

A broad reorganization of the ACS research program, aimed at stepping up the scientific attack on cancer, was announced on March 21, 1956. The Society's new program will include: *Program Grants*: which will be in two parts—one a commitment to support salaries of scientists up to five years; the other, an annual grant to defray costs such as equipment, supplies, and non professional salaries on a year-to-year basis. *Project Grants*: may be defined as the award of a specific sum of money made available to an institution for a limited period of time. They should be viewed as grants-in-aid. *Institutional Research Grants*: are allocations to qualified institutions to foster research—beyond that possible by project or program grants. *Contracts for Research*: to be governed by the nature and unique requirements of the job of work to be accomplished—designed to cover the type of activity not routinely performed by our institutions for higher learning, i.e., preparation in quantity of certain drugs or chemicals, development and standardization of a particular apparatus, etc. *Undergraduate Science Scholarship Grants*: to encourage deserving and qualified students, who would not otherwise do so, to enter college for the purpose of majoring in science. *Post-Doctoral Fellowship Grants*: to provide subsistence to young M.D.'s and Ph.D.'s over a limited period of time, so that they may amplify their previous training and experience to the point where they are able to conduct independent and productive research on some aspect of the cancer problem. *Grants for Additional Faculty-Level Positions for Scientific Investigators*: to deserving institutions for the purpose of making available additional permanent positions in those branches of

the biological sciences that are of importance to cancer research. *Grants for Scholars in Cancer Research*: to persons who need advanced training but who are assured of a suitable position after completing the scholarship, amount and term to be tailored to the individual needs of each grantee.

National headquarters of the American Cancer Society are at 521 West 57th Street, New York 19, N. Y.

THEODORE ADAMS

AMERICAN CERAMIC SOCIETY

The American Ceramic Society is an organization for the exchange of scientific information and for publishing papers on scientific and technical research in the ceramics field. Its members are from the wide variety of industries that produce useful objects from inorganic, nonmetallic materials, with manufacturing processes involving heat in the range of 700 F to 3000 F or higher. These include thousands of items ranging through brick and tile; glass of a thousand uses; porcelain enamels for kitchen, sanitary, chemical, heat resisting, and advertising purposes; abrasives, cements, limes and plasters, table ware, electrical porcelains, chemical porcelains, and refractories for lining metallurgical furnaces, jet engines, and refinery vessels.

Members of The American Ceramic Society are in eight divisions, Basic Science, Design, Enamel, Glass, Materials and Equipment, Refractories, Structural Clay Products, and White Wares. In addition the Society has two classes: the Ceramic Educational Council for the study of curricula in ceramic schools, and the National Institute of Ceramic Engineers.

An annual meeting of the Society each spring, division meetings each autumn and section meetings through the year provide opportunity for the presentation and discussion of technical papers on basic and applied research in the materials, processes and products of ceramic origin.

Publication of the more significant of these papers and others papers on current researches and developments of value to the ceramic industry is through the Society's three monthly publications. *The Journal of The American Ceramic Society* deals entirely with outstanding scientific papers on research in the ceramic field, presenting 75 to 100 papers annually. These papers include studies in analytical chemistry, crystal chemistry, colloid chemistry, solid state physics, instrumentation for high temperature reactions, as well as the development of specific ceramic materials. *Ceramic Abstracts* offers a broad reference and abstract coverage of the entire ceramic field, plus related coverage of geology, chemistry and physics. Every known publication on ceramic and related subjects, in this and foreign countries, is carefully studied for the more than 2800 abstracts published annually. *The American Ceramic Society Bulletin* is devoted to papers on the application of scientific material to daily operation of ceramic plants. It also carries articles of historical and general interest, news of the activities of the

Society, its branches and its members. In addition, the Society has sponsored the publication of numerous volumes of ceramic technical interest, including "Phase Diagrams for Ceramists," "Enamel Bibliography and Abstracts," "Bibliography of Magnesite Refractories," "Bibliography of Silica Refractories," and similar volumes.

The American Ceramic Society was founded February 6, 1899, at Columbus, Ohio, under the leadership of Edward Orton, Jr., founder and head of the first school for ceramics in the United States, at Ohio State University. Its first membership was of 15 "ceramic chemists or those who understand ceramic work from the scientific side and would be willing to share their information with fellow members." The Society has grown to more than 1,000 members, including many in 46 other countries.

Charles S. Pearce is general secretary of the Society, a position he has held since 1946. He has had extensive experience in the industry and is the author of numerous papers on enameling and porcelain.

The Society moved into its own building in Ceramic Park, at 1055 North High St., in Columbus, Ohio, in November, 1954. Construction of this office building and ceramic show place was made possible by more than \$100,000 in gifts from Society members.

JAMES S. WELCH

AMERICAN CHEMICAL SOCIETY

In April 1876, 35 chemists met in New York City to form an American Chemical Society. The first published list of members included 133 names. Originally the Society was incorporated in New York State by action of the 75th Congress of the United States, a national charter was granted effective January 1, 1938.

The objects of the Society always have been "to encourage in the broadest and most liberal manner the advancement of chemistry in all its branches; the promotion of research in chemical science and industry; the improvement of the qualifications and usefulness of chemists . . . the increase and diffusion of chemical knowledge; and . . . to promote scientific interests and inquiry; thereby fostering public welfare and education, aiding the development of our country's industries, and adding to the material prosperity and happiness of our people."

To serve specialized fields of chemistry, subject matter divisions are authorized. The first five were created in 1908; today there are 21. Geographic organization was conceived as a means of providing to the members in a relatively small area a program of activities beneficial to the science and the profession and readily available to participants. The first local section was formed in 1890; at the end of 1955 there were 149.

The Society as a whole has grown tremendously. At the end of 1955, there were 75,223 members, all meeting minimum standards of professional education and training. In addition, there were 4,839 student affiliates. At the first national meeting in

1890, 43 chemists were in attendance. Registration at the 126th National Meeting in September 1954 was 13,514.

The American Chemical Society owns and publishes the following, the date indicating time of establishment: *Journal of the American Chemical Society* (1879), *Chemical Abstracts* (1907), *Industrial and Engineering Chemistry* (1909), *Chemical and Engineering News* (then called the News Edition of *Industrial and Engineering Chemistry*) (1923), *Analytical Chemistry* (1929), *The Journal of Physical Chemistry* (1896), *The Journal of Organic Chemistry* (1936), *Journal of Agricultural and Food Chemistry* (1953). All except two of these were founded by the ACS. *The Journal of Physical Chemistry* was established by Wilder D. Bancroft and became the property of the ACS in 1933. It was not until 1952 that the Society also assumed the position of publisher. *The Journal of Organic Chemistry* was acquired in 1954 and the Society became publisher on January 1, 1955. In addition, the Society owns *Chemical Reviews*, published by The Williams & Wilkins Company. The Division of Chemical Education owns the *Journal of Chemical Education* and the Division of Rubber Chemistry owns and publishes *Rubber Chemistry and Technology*. (See *Chemical Literature*.)

The usefulness of *Chemical Abstracts* has been expanded through periodic publication of collective indexes of various kinds: Author, Subject, Formula, and Numerical Patent Index. In the "Advances in Chemistry" Series, the Society publishes specialized symposia and compilations of useful data. In 1943 Atherton Seidell assigned to the ACS the copyright of his "Solubilities of Inorganic and Organic Compounds." Subsequently the ACS published supplements and currently a complete revision is in progress. The work of the Committee on Analytical Reagents is reflected from time to time in a publication presenting specifications for reagent chemicals.

The first serious attempt to build up a chemical literature in English without primary regard to commercial considerations was begun in 1920 when the series of American Chemical Society Monographs was inaugurated. These books are published by the Reinhold Publishing Corporation, 430 Park Ave., New York 22.

The American Chemical Society is active in the educational field. Its first contact with students is with vocational counseling work at the high-school level. For the employed individual, continuation courses and special lecture series on specialized topics are sponsored by local sections. Between these two extremes are many other educational programs including the approval of departments in colleges and universities as qualified to give professional training.

Literally thousands of ACS meetings are held annually, including national, regional, local, divisional, and cooperative with other professional societies.

Professional matters are of great importance in the Society's program. Beginning in 1917 the work of the News Service has expanded gradually until today it is considered as an authoritative source of information for all those who disseminate in-

formation to the public—press, radio, television, magazines, books, etc.

The Society has increased the professional and economic status of chemists and chemical engineers through various procedures. It has extended opportunities for the profession; new jobs have resulted from its efforts. It maintains various kinds of effective employment aids. It has protected the chemist and chemical engineer against legal encroachments on their rights and has acted positively to gain recognition for their proper status.

The Society maintains effective liaison with all branches of the Federal Government. In certain cases advisory bodies to Government agencies are created. As a Federally chartered body, it has executed many assignments for the Government within its proper field.

The Society administers 19 awards and its local sections and divisions sponsor others.

The popular deliberative assembly of the Society is its Council. Each local section and each division is represented therein. Ex officio members consist of the President, the President-Elect, the Past Presidents, the Executive Secretary, the Treasurer, the Directors, and the Editor of each journal published by the Society. Total membership approximates 400.

The Board of Directors is composed of the President, the President Elect, the most recent Past President, six Regional Directors and four Directors-at-Large, and is the legal representative of the Society. The Constitution provides that it "shall have, hold, and administer all the property, funds, and affairs of the Society."

The Society is administered from headquarters at 1155 Sixteenth St. N. W., Washington, D. C. Four of its journals also are edited there. The staff of *Chemical Abstracts* occupies a building designed specifically for its use in Columbus, Ohio. The Editorial Offices for JACS and JPC and the staff for the Committee on Professional Training are in Rochester, New York. JOC is edited in Detroit. The ACS News Service is located in New York City. The four publications edited in Washington have full time staff representatives in New York, Chicago, San Francisco, Houston, and London. Production work is centered in Easton, Pennsylvania.

At the end of 1955, the full-time staff of the ACS, including its publications, numbered 312. Other persons are employed during peak periods or in special assignments. These figures do not include abstractors for CA, contributing editors, advisory boards, personnel in the advertising department, nor those engaged in printing; the last two are handled under contract. Local section, division, and committee personnel contribute hours of service equal in the aggregate to substantial staff increases.

ALDEN H. EMERY

AMERICAN DAIRY ASSOCIATION

The American Dairy Association is the dairy farmer's business voice in the market places

across America. It is a non-profit, non-brand, self-help organization financed, directed and controlled by the nation's dairy farmers. Its year around program activities include merchandising, advertising, research and public relations to increase the sale and use of milk and all dairy foods. The Association was founded in 1940 with a membership of six states and a budget of \$270,000. In 1954 its membership has grown to 45 states and a budget of \$5,000,000. Financing is accomplished by a year-around Set Aside, in most states voluntarily, on the basis of one-half cent per pound of butterfat or two cents per hundredweight of milk delivered at the dairy plants. The advertising program covers national consumer magazines, metropolitan newspapers, restaurant publications, trade journals and farm publications. National network radio broadcasting and TV is employed. Its merchandising activities include month-by-month, product by product festivals (merchandising events) with tie in promotions by manufacturers of related foods, dairy product distributors and retail outlets.

Research activities include financial support of specific projects on problems related to increased sales of dairy products. On the scientific side, projects are placed at universities, experiment stations, laboratories, medical colleges and research centers. On the market side, consumer studies and interview surveys are supported and encouraged with the nation's leading market research organizations.

Public relations activities include a regular recipe release service from the Home Service Department to food editors of metropolitan newspapers, national consumer magazines, radio and television. Public relations also stresses feature and news information to the press, radio and television in addition to conducting editorial forums.

LESTER WILL

AMERICAN DRY MILK INSTITUTE

The American Dry Milk Institute was organized in 1925 to do research and educational work into nonfat dry milk solids. Research includes: (1) Technical research on standards and grades, methods, sanitary and quality code, packaging. The standards, grades, and methods developed have been adopted by all government agencies. (2) Product research into new uses, methods of use, established uses, nutritional contributions. (3) Market research on distribution, sales, end use, trends, potentials.

The Institute maintains a laboratory which provides facilities for industry control and research. The principal area of research covered by the laboratory is chemical analytical methods. Since 1935, the laboratory personnel have published frequently in the *Industrial and Engineering Chemistry*, *Journal of Association of Official Agricultural Chemists*, *Journal of Dairy Science*, *Cereal Chemistry*, and *Journal of Milk and Food Technology*. In addition to the chemical and bacteriological laboratory, the Institute also maintains a bakery laboratory in which it studies application

of milk products to baked goods. Since its founding, the Institute has maintained annual fellowships and grants-in-aid at universities throughout the country on one or more phases of dry milk and its relation to the food industry.

Translating potentialities into practical achievements through market development, the Institute renders direct customer service through a technically trained field staff, carries advertising and publicity in trade and professional papers, distributes publications, press releases, etc. It is constantly alert to all legislative activity related to dry milks in order to quickly mobilize industry strength in support of interests. Governmental contacts are constant, constructive and productive. Teamwork of Government and Industry through ADMI has aided in quality and scientific development; increased production, improved packaging, storage, and distribution; expanded use; and has achieved better understanding of the nutritional contribution of dry milks.

Production has grown from 73 million pounds in 1925, at the time the Institute was organized, to 1¼ billion pounds in 1955. New and expanded markets are needed, and the Institute continues its research and market development efforts toward this end.

DOROTHY McCANN

AMERICAN INSTITUTE OF BAKING

In 1897, the newly organized baking industry of the United States chose as its first honorary member—a chemist. It was at this meeting too that the idea of a scientific and educational center of the industry was proposed. When the American Institute of Baking was founded twenty-two years later, its initial activity was laboratory research and service. Through the years, the plan for linking the American Association of the Baking Industry with research, and also with training in baking technology, was discussed at each meeting of the Association. In May of 1918, a plan was submitted to finance the establishment of an institute. A director, Harry E. Barnard, and staff, C. B. Morison and Peter Pirrie, were secured in the fall of 1919, and research and service laboratories were opened in rented quarters in Minneapolis.

Activities of the institute became of such direct service to the industry and the possibilities for the expansion of research, service and educational activities became so apparent that plans were made for enlarged facilities. The Wahl-Henius Institute was purchased, and all equipment, personnel and activities were removed from Minneapolis to 1135 Fullerton Avenue, Chicago. The School of Baking opened in 1922 in the new headquarters, and the former Wahl-Henius library of fermentation became the nucleus of the Louis Livingston Library of Baking. Some years later a department of nutrition was established in New York City, with Dr. James A. Tobey as its director. This work later was expanded into the Consumer Service Department of the Institute, and upon the closing of the New York branch, test

kitchen and offices for the department were opened in Chicago. Fifth of the major departments of the Institute, the Department of Bakery Sanitation, was organized in 1945 at the request of the baking industry.

For almost 29 years, the Institute functioned at the headquarters on Fullerton Avenue, continually expanding its services both to the baking industry and to the consumer. For the six year period 1943-1949, Dr. Franklin C. Bing, eminent nutritionist, was director of the Institute. In 1948, the Board of Directors of the Institute decided to purchase property for the erection of a new building. A site at 400 East Ontario Street, in the heart of Chicago's hospital and university area, was acquired. The new building was dedicated in October, 1950.

The funds which made possible the new facilities and the development of an enlarged program of research, service and education were by subscription in the industry itself. The larger part of the machinery and equipment and laboratories has been consigned, loaned or donated by bakery equipment manufacturers, or as a memorial to some bakers' association, group, company, or individual.

Investigation of food poisoning problems is an example of the type of project financed by the general funds of the Institute. The Sugar Research Foundation sponsored a study of the function of sugars in bread. An investigation of the bacteriological characteristics of pineapple cream fillings was financed by the Pineapple Growers Association.

Since 1948 the Institute has been studying bread-staling, a project financed mainly by funds from the Department of Agriculture, and to some extent by the general funds of the Institute. During 1952 a third phase of the project was completed.

While research is the primary function of the laboratories, the department has an important role in the education and service activities of the Institute. Educational contributions also are made by the publication of articles in technical or trade journals, and of special laboratory bulletins. Finally, there is the analytical section, which has been designed primarily as a service laboratory for bakers. Subscribing firms submit samples of ingredients or finished products for analysis. From a laboratory examination of flour, it is possible to determine the best way of handling the flour to produce a good loaf of bread.

Late in 1952 the laboratories were granted a half million dollars by the Max C. Fleischmann Foundation, to be transferred to the Institute at the rate of \$50,000 per year. This will enable the Institute to continue its study of the staling phenomenon, which previously had been conducted on a contract basis in limited areas of investigation.

The Institute's programs in scientific research are under the guidance of William B. Bradley, scientific and research director of the Institute, with Welker G. Bechtel as director of laboratories. A staff of twelve, including research and analytical chemists, research bacteriologists and nutritionist, and baking technologists, works on the

service and research projects. Fifteen well known scientists lend their professional help to the laboratory investigations, and hold regular meetings at the Institute.

Howard O. Hunter is President of the Institute, and its other officers are Louis E. Caster, chairman of the board; Milton Petersen, vice chairman of the board; Joseph A. Lee, treasurer; and Paul Chapman, secretary. A board of directors is composed of men of the baking industry and allied trades.

The American Institute of Baking is an Illinois corporation not for profit. It is financially supported in several ways: by membership dues; by fees of departments such as the School of Baking and the Sanitation Department; by grants for research project and by payments from the Bakers of America Program for services rendered in Consumer Service.

R. I. TENNEY

Fermentation in Breadmaking

Flour was made in stone mills until about 1880, when roller mills permitted the development of various grades of flour superior in bread making properties. The production of a uniform type of compressed yeast of good keeping quality and good quality protein flour enabled the bakers to standardize their procedures. These advances made the development of commercial bakeries possible. At present it is estimated that 90 per cent of the bread consumed in the U. S. is produced by bakers.

Leavening of doughs by means of yeast is a biological process. The dough is made by mixing flour, water, yeast, and usually sugar, salt, shortening, and nonfat dry milk. Enzymes and dough conditioners may be added.

Recently the Food and Drug Administration defined white bread, enriched bread, and various other types of bread, and issued standards. There are many different types of bread, such as hearth, pan, and rye bread, but breads of these types are produced by using yeast as a leavening agent. The sugar developed by the enzymes generally present in flours, as well as the added sugar, is partly utilized by yeast to produce alcohol and carbon dioxide, the latter producing aeration. Actually, the action of yeast in the fermenting dough is not fully understood, for in addition to carbon dioxide production, other reactions take place: the dough becomes acid; the properties of the gluten are altered; there may be some action during fermentation on flour proteins and the starches are modified. This action is known as "conditioning." It is a dynamic process. It involves chemical changes in sugars, starches, amino acids, proteins, and enzyme systems. Many of these conditioning reactions, such as the action of added oxidants on gluten and the metabolic activity of yeast in doughs, have defied complete analysis.

In the United States bread is mainly produced by two methods, the straight dough and the sponge dough. In the former, all the ingredients

are added at one time, and the yeast in amount of 1 to 3% is allowed to ferment at about 80 to 85°F with controlled humidity until the dough is properly aged or conditioned. It is then sent to the divider, cut, weighed, rounded, and allowed to ferment for 10 to 20 minutes in the overhead proof. The dough units are then passed into the moulder, and the moulded dough is placed in pans, and proofed for 60 to 70 minutes at 95 to 100°F. The dough rises rapidly, and when it reaches the top of the pan or slightly above, it is sent to the oven and baked at 375 to 450°F.

The sponge process is generally carried out by adding 60% of the flour and water to be used with yeast, diastatic enzymes, dough conditioners, and part of the salt, mixing, and fermenting at 76 to 78°F with controlled humidity until the sponge is properly conditioned as indicated by the character of the dough and the collapse of the sponge. The sponge is then returned to the mixer to be mixed with the remaining yeast, making a total equivalent to 2 to 3%; the remaining flour, salt and water are added, together with other ingredients which are generally included in the final dough, such as shortening, sugar, and nonfat dry milk. The dough usually ferments for 10 to 40 minutes at 84 to 85°F, and is then treated like a straight dough: cut and weighed by the divider, rounded, fermented 10 to 20 minutes, moulded, panned and allowed to rise in the proof at about 100°F until the dough rises to the level of the pan or slightly above. The dough loaves are then placed in the oven and baked at 425°F, or slightly higher, for 30 minutes and then cooled. The fermentation continues in the oven until the temperature reaches approximately 144°F, when it ceases, but the gases continue to expand the dough until the gluten coagulates and the gas escapes.

A number of factors influence the volume, loaf character, flavor, and odor of bread. Bread made without fermentation has no flavor except that of the flour. A large amount of yeast gives a distinctive character to bread. Ethyl alcohol, aldehydes, acids, and ketones are produced during fermentation, and they influence flavor and odor of freshly baked bread. Certain dry yeasts are "proteolytic" and have a strong reducing action in doughs, changing the flavor and crumb structure. Glutathione is apparently involved as a factor. Thiamine, ammonium ions, amides, and amino acids, if present in doughs, accelerate the rate of fermentation, and may thus influence the volume and internal characteristics of the loaf. Mineral salts of phosphates, magnesium, potassium, and sulfates are necessary for fermentation. These salts and thiamine are usually present in wheat flour.

The rate of fermentation is an important factor in developing a dough. Most bakers use from 1½ to 3% yeast. Yeasts grown on cane or beet molasses often ferment at decreased rates when confined to fermenting maltose produced by the enzymes of the flour. There is usually a lag period of 20 to 30 minutes following the fermentation of the preformed sugar, sucrose, and levosin present in flour; during this time the yeast adjusts its rate, finally fermenting nearly at the rate it attains on cane sugar. Glu-

cose and cane sugar ferment at approximately the same rate. The enzyme invertase converts cane sugar to dextrose and levulose. Yeast selectively ferments dextrose in a mixture of the two sugars. As a result, levulose is usually present in larger amounts than dextrose in the baked bread.

Sensitivity of yeast affects the fermentation rate. Some yeasts are affected by the salt concentration which may reach 2 to 2½ per cent in certain doughs. Osmosensitivity of certain yeasts may not be confined to salt alone, but sugar sensitivity may also be involved; 2½ to 5% of alcohol perceptibly depresses the fermentation rate of certain yeasts. Levels of 1 to 3% may be produced in doughs by fermentation.

The temperature in dough fermentations is an important factor. Doughs are usually fermented at temperature ranges of 75°F in the dough to as high as 100°F in the proof box. The yeast continues to ferment in the oven at higher temperatures. The more resistant the yeast is to inactivation at low or high temperatures, the greater is its effective working range and ability to produce a well leavened loaf. Inhibiting substances which decrease the rate of fermentation are present in varying amounts in wheat flour. Balls has isolated a substance, purothionin, which is toxic to yeast.

A large amount of fundamental work will be required before the basic reactions involved in the leavening process can be fully controlled or followed.

CHARLES N. FREY

Cross-references: *Enzymes, Foods, Antibiotics*

AMERICAN INSTITUTE OF BIOLOGICAL SCIENCES

Organized in February 1948 under the sponsorship of the National Research Council, the Institute became independent in January 1955, when it was incorporated in the District of Columbia. Offices are now located at 2000 P Street, N.W., Washington 6, D.C.

The Institute is a voluntary association of professional biological organizations and individuals who share a common interest in the life sciences. The specific aims of the Institute include (1) assistance to biological societies and similar organizations in matters of common concern which can be dealt with most effectively by united action; (2) promotion of unity and effectiveness of effort among all who are devoting themselves to the biological sciences by research, by teaching, or by application of biological data; (3) furthering the relationships of the biological sciences to other sciences and to the arts and industries; and (4) cooperation with local, national, and international biological organizations.

The official publication of the Institute, *The A.I.B.S. Bulletin*, serves as a medium of inter-society communication, a source of general biological news and information, and a forum for the discussion of subjects of general interest to biologists.

Arranging for national meetings of A.I.B.S. societies and other societies who request such

service is another important aspect of the A.I.B.S. program. This program also includes a Placement Service offering a liaison service between biologists and prospective employers, a business office service including the maintenance of society addressograph files, and representation of biology with the Federation of American Societies for Experimental Biology, on the Scientific Manpower Commission. In addition, the A.I.B.S. cooperates with the National Science Foundation in the distribution and coding of questionnaires and the compilation of statistical data for the National Register of Scientific and Technical Personnel, and assists the Office of Naval Research in evaluating the scientific merit of research proposals in biology, biochemistry, physiology, and physiological psychology through select advisory committees. Special conferences are arranged and consultants appointed in various biological fields of interest to the Office of Naval Research.

Many other projects are undertaken by A.I.B.S. as a service to biologists. A Publications Committee is most active in surveying problems that exist in abstracting, indexing, research publications, evaluating new methods of rapid communication and activating programs in these areas. A new Committee on Basic Biological Research on Ageing has been formed and a Committee on Biological Education and Recruitment will be functioning by September 1955.

IRVIN C. MOHLER

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The American Institute of Chemical Engineers was founded on June 22, 1908, in Philadelphia, Pennsylvania, by a group of forty eminent chemical engineers. Growth of the engineering side of the chemical industries was constant but slow for the next thirty years as the pioneers searched out principles and formulated their application to the field. With the ever increasing demand for the manufacture of plastics, fuel, clothing, foods, and housing, the profession grew rapidly. In 1955, the Institute had as members over 15,000 chemical engineers, most residing in the United States.

As defined by the Constitution of the A.I.Ch.E., the purpose of the A.I.Ch.E., which is the largest society in the world devoted exclusively to the profession of chemical engineering, is "the advancement of chemical engineering in theory and practice and the maintenance of a high professional standard among its members." Chemical engineering is "the application of the principles of the physical sciences, together with the principles of economics and human relations, to the fields that pertain directly to process and process equipment in which matter is treated to effect a change in state, energy content, or composition."

Seventy-five per cent of the A.I.Ch.E. income is spent on publications and support of basic literature in the field.

Two magazines, *Chemical Engineering Progress* and the *A.I.Ch.E. Journal*, are issued regularly. From 1908 to 1935 a single yearly volume was pub-

lished; in 1935 the publication became a bi-monthly, to be superseded in 1947 by the monthly *Chemical Engineering Progress*.

Chemical Engineering Progress is the official publication of the A.I.Ch.E. As such it carries official notices and news of the organization, but the main function of the magazine is to bring to the chemical engineer technical articles of major importance in the production, management, development, and sales phases of chemical engineering. The *A.I.Ch.E. Journal* was begun as a quarterly in March, 1955, and is dedicated to the basic science of chemical engineering. Both magazines have access to the papers presented at the four meetings held every year by the chemical engineers.

In addition, the Institute also publishes the *Chemical Engineering Progress Symposium Series*—an inexpensive series of collections of papers on theoretical and experimental developments of importance to chemical engineers—and the *Chemical Engineering Progress Monograph Series*, extensive treatises in the chemical engineering field covering many diverse subjects. The Institute also publishes a directory of chemical engineering faculties in the United States and Canada, a roster of its members, a guide of engineering films for industrial and student use, a compendium of chemical engineering problems for students.

The A.I.Ch.E. has many committees working in many different fields. One of these is the *Chemical Engineering Accrediting Committee*, which is the Institute's authority on the status of chemical engineering education. Its inspecting groups are accepted and welcomed by institutions throughout the United States for examination and evaluation of their chemical engineering courses.

Cooperation with other groups is also an important part of Institute activities, and to this end the A.I.Ch.E. in conjunction with other associations advises on the issuance of standards, on the maintenance of documentary sources, and on engineering education, safety, and corrosion problems. The Institute is represented on the National Research Council and on various engineering cooperative organizations.

Annually the Institute makes three major awards—the William H. Walker Award and the Junior Award, both given for contributions to chemical engineering literature, and the Professional Progress Award in Chemical Engineering, sponsored by the Celanese Corporation of America, Inc., and administered by the A.I.Ch.E., for individuals under forty-five years of age whose achievements are of major importance to the profession and who thus have made a significant contribution to the science of chemical engineering.

Membership in the Institute is of four grades: Member, Associate, Affiliate, and Student. Membership requirements for full grade, or Member, are rigid, requiring at least six years' experience after a first degree in chemical engineering is received and at least three years of responsible charge of important chemical engineering work. Associates must have both chemical engineering education and experience; Affiliates must be in work which enables them to cooperate with the

profession; and a Student must be enrolled in a curriculum leading to a degree in chemical engineering.

A.I.Ch.E. policies are executed by four elected officers—president, vice-president, secretary, and treasurer—and the most recent past president. Policy is set by a Council of seventeen, including twelve directors, four officers, and the past president. Officers are elected for a term of one year; members of Council serve overlapping three-year terms.

The Institute has fifty-one local sections in the United States, and student chapters are encouraged in schools and universities throughout the world. It sponsors a yearly contest open to under graduate chemical engineering students.

The address of the A.I.Ch.E. is 25 West 45 Street, New York 36, New York.

F. J. VAN ANTWERPEN

AMERICAN INSTITUTE OF CHEMISTS

Founded in 1923 by a small group of far-seeing chemists and chemical engineers who dedicated themselves to doing something about professional matters. They looked to the development of the then young chemical industry in the United States which needs the full, unhampered creativeness of chemists and chemical engineers. As professional consciousness increases among scientists, their power to create and to accomplish is increased; a favorable environment for creative minds is provided. The AIC is therefore concerned with chemists and chemical engineers as professional people, not with the science of chemistry as such, because a science cannot advance save through the superiority of those in it. Special stress is placed on the scientific integrity of the individual and a Code of Ethics is adhered to by AIC members.

Qualifications for membership require adequate education and professional experience. Fellows must have a degree in chemistry or chemical engineering from an accredited school, plus at least ten years of progressive experience; Members must have the degree and a minimum of four years of experience; Associates have the degree but need not have experience.

The objectives of the AIC are (1) to provide and enforce the code of principles of professional conduct which merits public esteem and justifies confidence in the integrity of the chemist or chemical engineer; (2) to establish and maintain a standard of proficiency of such excellence as to insure competent and efficient service; (3) to secure an adequate basic training for the professions and to admit to fellowship in the Institute only those of proved education, experience, competence and character; (4) to enhance the prestige and distinction of the professions and to extend their influence and usefulness; (5) to establish and maintain a register of membership in which there shall be a complete record of the training, experience and fitness for service of each member; (6) to improve the economic status of the profession by cooperating with employers to secure a satisfactory appreciation and evaluation of the services of the chemist and chemical engi-

neer; (7) to provide means for appropriate recognition of distinguished service rendered by individual members of the professions; (8) to cooperate with all agencies serving chemistry to make the professions of chemistry and chemical engineering powerful factors in the advancement of intellectual and material progress in the United States; (9) to support the work of the chemical and chemical engineering societies in the education of the public to a better appreciation of the contribution of the chemist and chemical engineer to world progress; (10) to render such other services to the profession as developments shall warrant and of which The American Institute of Chemists shall approve.

The AIC functions through a Board of Directors, made up of the four officers, nine councilors-at-large, and the immediate past president; and through a Council consisting of the four officers, nine councilors-at-large, the two immediate past presidents, and a representative from each of its twelve chapters. Certain committees are specified in its constitution to handle professional matters, such as employer-employee relations, national legislation affecting chemists, professional education, patents, employment contracts, and ethics. Other committees are appointed by the Council. The chapters of the AIC are Alabama, Baltimore, Chicago, Louisiana, New England, New Jersey, New York, Niagara, Ohio, Pennsylvania, Washington, D. C., and Western.

The AIC publishes *The Chemist*, a monthly journal containing articles on professional subjects, career information, news, employment needs, new chemical literature announcements, and other departments. Many of the articles in *The Chemist* are distilled directly from the observations and experiences of the authors, and are a significant contribution to the literature of the professions. Reports of committees are also published in *The Chemist* and are often reprinted. A directory of the membership is published every three or four years.

The AIC awards a gold medal annually for noteworthy and outstanding service to the science of chemistry or the profession of the chemist or chemical engineer in America. Recent medal recipients are Raymond Stevens (1956); Dr. Carl S. Marvel (1955); Dr. William J. Sparks (1954); Dr. J. C. Warner (1953); Fred J. Emmerich (1952); Dr. Harry N. Holmes (1951); Walter J. Murphy (1950); Dr. Warren K. Lewis (1949); Dr. Charles A. Thomas (1948); Dr. M. L. Crossley (1947).

The present (1956) officers of the Institute are: Dr. Ray P. Dinsmore, president; John H. Nair, president-elect; Dr. Lloyd Van Doren, secretary; Dr. Frederick A. Hessel, treasurer, and Dr. Donald B. Keyes, chairman of the Board of Directors. The membership is about 3000. The organization's headquarters are at 60 East 42nd St., New York 17, N. Y.

VERA F. KIMBALL

AMERICAN INSTITUTE OF LAUNDERING

Now located in Juliet, Illinois, the American Institute of Laundering dates back to October,

1883, when the Laundryowners National Association was formed in Chicago by some 50 laundry-owners from 17 states. The purposes of the American Institute of Laundering are threefold: (1) To coordinate all scientific endeavor in connection with the laundry industry and to disseminate by various media, scientific data and other pertinent information to the members of both the American Institute of Laundering and to professional and local laundry association secretaries. (2) To train students in the scientific application of laundering. (3) To maintain a model commercial laundry equipped with the most modern machinery and operated as profitably as possible, employing the latest improvements for quality and production.

In its efforts to provide laundrymen with the technical know-how and help so necessary to keep pace with today's changing trends, a variety of services are offered by the Institute. The A.I.L.'s model laundry is operated as a practical industry proving ground, and from years of study have come a wealth of information. While production problems have a way of popping up unexpectedly and urgently need practical help, Institute staff-men have found that the great majority of problems prevalent throughout the industry have been experienced at one time or another in their own model laundry. As a result, past experience enables the A.I.L. staff to be of considerable help in solving the individual laundryman's problems.

The American Institute of Laundering offers a variety of services to its members. Two of the most popular are the test piece service for controlled washrooms and the fabric analysis service. Through the use of the test piece, a laundry-owner can be positive that his supplies and washing formula are the best for his conditions. It assures him that his washing procedure is one that will best prolong the life of his customers' clothes and wash them thoroughly clean, while still maintaining their tensile strength and whiteness.

The A.I.L. Fabric Analysis reports have been universally accepted as valid by courts, insurance companies, textile manufacturers, retailers, laundries and their customers. There is no limit to the number of pieces any laundry may send in in the course of a year, and for the past several years, the number of pieces has reached about 5,000.

One of the most popular divisions of the A.I.L. is its school of laundry management. Actually it is a university of laundering, and it is the industry's only school adequate to fill the increasing need for trained management personnel. Concentrating on the practical laundry management approach, courses are offered in production engineering and management, and in sales and financial management.

LEE G. JOHNSTON

AMERICAN INSTITUTE OF MINING, METALLURGICAL, AND PETROLEUM ENGINEERS

The first meeting of the American Institute of Mining and Metallurgical Engineers was held in Wilkes-Barre, Pennsylvania in 1871. As originally

organized, "Metallurgical" and "Petroleum" were not a part of the name, although from the very beginning metallurgists were emphasized in the society's plans. The official abbreviation is AIME.

The objectives of the society as expressed in its constitution are: "To promote the arts and sciences connected with the economic production of the useful minerals and metals, and the welfare of those employed in these industries by all lawful means." The first period in the history of the Institute lasted forty years. It was marked by a uniform growth in membership of about 100 members per year. During this period one man, Dr. Rossiter W. Raymond, stood out as a dominant, wise and beneficent leader. He planned meetings of varied interests and was responsible for building a high standard of scientific, technological and editorial excellence in the Institute's *Transactions*.

During the first decade of this century the AIME, together with societies representing mechanical, electrical and civil engineers, accepted a gift of just over a million dollars from Andrew Carnegie. This money, together with funds of their own, permitted them to build a 16 story Engineering Societies Building at 29 W. 39th Street in New York City for their various headquarters offices. Included is an outstanding engineering library open to the public. With members in every state and in most foreign countries local sections have been organized in the last forty two years more effectively to carry out the purpose of the Institute. Sixty seven local sections had been organized by February 19, 1956, of which four are outside the United States.

The American Brass Founders Society, organized in 1907, and subsequently changing its name to the American Institute of Metals, joined with the AIME in 1918 to become the Institute's first Division. It was at this time that "Metallurgical" became part of the full name of the Institute. Originally the Institute of Metals Division concerned itself with nonferrous physical metallurgy. In 1948 its field was broadened to include all physical metallurgy. The Iron and Steel Division, formed in 1928, now confines itself to iron and steel production, including the working of steel, but not other physical metallurgy. The Petroleum Division became the second Division of the Institute in 1922. It concerns itself with production but not refining. Since these three Divisions were formed seven others have been added: Coal, Mineral Industry Education, Industrial Minerals (nonmetallies), Minerals Beneficiation, Extractive Metallurgy (nonferrous), Mineral Economics and finally Mining, Geology and Geophysics the largest of the ten. "Petroleum" was added to the name in 1956.

Eight of the Divisions have been grouped into three Branches. The Petroleum Division constitutes one Branch, with its own office at 800 Fidelity Union Building in Dallas, Texas. The Mineral Economics and Mineral Industry Education Divisions are Institute-wide with representation in all three Branches. The Institute of Metals, Iron and Steel and Extractive Metallurgy Divisions constitute the Metals Branch and the other

four Divisions the Mining Branch. Approximately half of the membership is in the Mining Branch and one fourth in each of the other two.

Prior to 1949 one monthly Journal, *Mining and Metallurgy*, was sent to all AIME members. Separate publications containing technical papers were sent to appropriate groups in the Institute as follows: *Mining Technology*, bi monthly; *Petroleum Technology*, bi monthly; *Metals Technology*, semi-quarterly; and *Coal Technology*, quarterly. Since 1949 each Branch has had its own monthly publication, *Mining Engineering*, *Journal of Metals* and *Journal of Petroleum Technology*. The other periodicals have been discontinued and the technical papers form the *Transactions* Section of the respective monthly Branch journals. The Branch setup with three journals was developed because there is little community of technical interest between members of the respective three Branches. At the end of the year overruns of the *Transactions* Section of each journal are bound as the AIME Transactions volume for that Branch. They thus provide an indexed, permanent record of the papers most likely to be referred to in future years.

Most of the papers in the *Transactions* Section of the journals are presented by the authors at Annual Meetings of the Institute in February. In even years about 3500 members of all Divisions attend such meetings in New York City. In odd years the meetings are held in various midwestern or farwestern cities. Most of the Divisions also hold one or more other national or regional meetings during the year. The Iron and Steel Division has four technical committees: Open Hearth Steel, Electric Furnace Steel, Bessemer Steel, and Blast Furnace, Coke Oven and Raw Materials which hold national meetings. Except for the Bessemer Committee, these are three day meetings resulting in printed and bound Proceedings distributed to the 300 to 1200 attending each meeting and for sale to others.

Besides the local section meetings mentioned before, 72 student chapters have been formed to serve the mineral industry students and acquaint them with the functioning of professional societies upon which they will become dependent for most of their technical information after their college educations. Such information will come to them through the various publications mentioned above and technical books published by the Institute, through oral presentation of papers at various meetings and personally from friends in similar positions to theirs whom they meet at Institute meetings.

The Institute has many awards which are made each year. Several are made to recognize outstanding achievement in various fields embraced by the Institute. Another group of awards given each year are presented for the best technical papers published by the Institute in various fields, some to young men exclusively. The Woman's Auxiliary of the AIME maintains a scholarship and loan fund to help needy students in the mineral industry field.

On December 31, 1955 there were 14,918 Members, 2,612 Associate Members, 6,127 Junior Mem-

bers and 2,825 Student Associates. A Member must be 27 years of age and have six years experience in the engineering profession of which three years must have been in responsible work. Engineering is broadly defined to include applied chemistry and other sciences. Associate Members need only have an interest in the engineering profession. Junior Members must be under 30 years of age when elected and qualified to hold a subordinate engineering position. Student Associates must be full time undergraduate or graduate students in approved schools.

E. O. KIRKENDALL

AMERICAN INSTITUTE OF PHYSICS

The American Institute of Physics is a federation of five national scientific societies in the field of physics. These are the American Physical Society, devoted to the advancement of all branches of fundamental and applied physics; the Optical Society of America, devoted to the science of optics; the Acoustical Society of America, devoted to the science of acoustics; the Society of Rheology, devoted to the science of deformation and flow of matter; and the American Association of Physics Teachers, devoted to the pedagogical and cultural aspects of physics. The Institute was founded in 1931.

The Member Societies vary in size from 400 to 12,000 members. They hold frequent scientific meetings for the presentation of technical papers and informal exchanges of information. They publish, through the American Institute of Physics, *The Physical Review*, the *Reviews of Modern Physics*, the *Journal of the Optical Society of America*, the *Journal of the Acoustical Society of America*, *Noise Control*, *American Journal of Physics*, *The Review of Scientific Instruments*, *The Journal of Chemical Physics* (of considerable interest to many chemists), the *Journal of Applied Physics*, *Physics Today* and *Soviet Physics JETP*.

Each of the Societies is autonomous, and is governed by an executive council and the usual officers. The Societies and their members elect the Governing Board of the American Institute of Physics.

The Institute publishes the journals and meeting programs, assists in secretarial, financial and legal matters; operates a placement service; presents physics in cooperation with other associations and in various national councils; assists the Federal Government with information, advice and the administration of specific projects on contract; and has general concern with public relations, the integrity of the field of physics and the development of needed income, etc. Many chemists are included in the membership of these groups and many technical papers at meetings have a close bearing on chemistry as well as physics. Nearly every issue of the journals contains articles of value to chemists. 36 per cent of all physicists are employed in industry and of these from 15 to 20 per cent are employed in industries primarily chemical in nature.

In addition to the Member Societies, there are a

number of Affiliated Societies, including the Electron Microscope Society of America, the American Crystallographic Society and a number of local associations.

HENRY A. BARTON

AMERICAN IRON AND STEEL INSTITUTE

The American Iron and Steel Institute is a non-profit New York membership corporation, organized in 1908 to succeed the American Iron and Steel Association, which traces back to 1855. As of January 1954, the Institute had 98 company members and 2500 individual members. Ninety of the company members were in the United States, four in Canada and one each in Argentina, Brazil and Chile. Membership has always been restricted to Western Hemisphere nationals. The 90 company members located in the United States included four companies engaged primarily in the production of pig iron. The other 86 companies operate 292 plants in 195 communities and have the capacity to produce almost 95 per cent of the country's steel.

Management of the affairs of the Institute is in the hands of the Board of Directors, each member of which has one vote on any matter which comes before it for action. The Board membership now includes 30 executives from 30 different companies, which in the aggregate comprise the major part of the industry. The officers of the Institute are elected by the Board of Directors, and are directly responsible to the Board of Directors. Directors of the Institute are elected by the active and company members, although vacancies on the Board may be filled by a majority vote of the remaining Directors. Candidates for election to the Board are selected by a Nominating Committee, which itself is elected by the active and company members.

Among the major activities of the Institute are various types of technical and engineering work, the compilation and dissemination of industry-wide statistics, the distribution of information about the industry to the public, and discussion of problems in the field of industrial relations including health and safety. The principal purposes of the Institute, as outlined in its constitution are: (1) to promote the interests of the iron and steel industry or any part or branch thereof, (2) to collect statistics and other information concerning the industry, (3) to engage in investigation and research, (4) to provide a forum for the exchange of information and discussion of problems relating to the industry, and (5) to promote the use of iron and steel.

The major activities of the Institute are carried on by some 55 committees having over 650 members. The membership of the committees is drawn from the staffs of the company members, each individual member being expert in the field of the committee's major interest. A staff member of the Institute is assigned to each committee; four staff members are registered professional engineers in one or more states. Many others have specialized technical training.

Of primary interest in the fields of steel technology and metallurgy are the committees in the division of Operations, Technology and Research. Headed by the Committee on Manufacturing Problems the division embraces committees which study primary processes (blast furnaces, coke ovens, electric and open hearth furnaces, and refractories); those which, under the direction of the General Technical Committee, study finished steel products (carbon and alloy steel bars, electrical steels, sheet steel, stainless steels, tool steels, railroad and structural steels, etc.); and, a Committee on General Research which supervises the research program of the Institute.

Space will not permit a complete statement of the chemical and metallurgical studies and researches pursued under the auspices of various Institute committees. The following will typify much of the work.

The control and possible utilization of industrial wastes is under study at Mellon Institute and Kettering Institute of Applied Physiology, particularly the reactivation or recycling of waste pickle liquors, and the elimination of phenol. The problems peculiar to the steel industry embraced by the general field of air pollution abatement are being studied at the Air Hygiene Foundation of America, Inc. at Mellon Institute and the Harvard School of Public Health. Extensive studies have been made of the types of sinter, their chemical and petrographic constitution and the best methods of evaluating their performance in the blast furnace. Those studies were conducted at Mellon Institute.

In the field of the physical chemistry of steel-making studies on slags are being pursued at Massachusetts Institute of Technology and Carnegie Institute of Technology. The mechanical, physical and chemical properties of carbon as a blast furnace lining have been studied at Armour Research Foundation. Studies have been conducted at the Pennsylvania State University and Massachusetts Institute of Technology on refractory phase diagrams. Work on the recovery of manganese from open hearth slags and low manganese content ores has been pursued at the Bureau of Mines Experiment Station at College Park, Maryland, and at Pittsburgh. A chemical method has been under study at the Armour Research Foundation.

At Battelle Memorial Institute studies are continuing toward the production of iron of the highest possible purity in substantial quantities, in order to assist research workers in developing information concerning both pure iron and alloys of exceptional purity, especially at extremes of temperature. Some work has also been done at the University of Pennsylvania. The Institute has cooperated with the Alloys of Iron Research Committee of the Engineering Foundation in an endeavor to place before the public books concerning the effects of the various alloying elements of steel, and has pursued research on zirconium as a substitute for manganese at Southern Research Institute.

Work has been done at the Case Institute of Technology on the zinc-iron couple, particularly

as applied to galvanized pipe. Field tests on chemical treatment for corrosion control of steel pipe are in process, and in one project, information on services with silicate treatment was compiled for a period of more than ten years. Work has been pursued at Armour Research Foundation which has resulted in the development of a substitute for palm oil in the hot-dip tinning process, and as a lubricant in the cold-rolling of steel. The Institute also cooperates with the National Bureau of Standards in its standard chemical samples program.

The research projects sponsored by the Institute are those which cannot be regarded as competitive; rather the subjects are those that might be utilized on a common basis throughout the iron and steel industry or a large part of it.

CHARLES M. PARKER

AMERICAN METEOROLOGICAL SOCIETY

The American Meteorological Society was organized in affiliation with the American Association for the Advancement of Science at St. Louis, Mo., on December 29, 1919, and incorporated at Washington, D. C., on January 21, 1920, with the object of "the development and dissemination of knowledge of meteorology in all its phases and the advancement of its professional ideals." In addition to its affiliation with the A.A.A.S., the Society is affiliated with the National Research Council of the National Academy of Sciences, and is represented both on its Division of Physical Sciences and on the Division of Earth Sciences.

Increasing interest in meteorology is evidenced by a steady increase in membership over the years, the numbers having grown from 2200 in 1916 to over 5700 at present. There are various types of membership in the Society. Corporation membership is open to organizations interested in the advancement of meteorology, and members in this category include private weather consulting firms, airlines, utilities, business, industrial and research organizations, and university departments of meteorology. An individual who possesses special qualifications in meteorology may become a Professional Member, the status appropriate to those who are actively engaged in meteorology as a profession. Persons whose interests or activities in meteorology or climatology would make them desirable members of the Society may apply for Member status. This affiliation also fills the needs of those who are not yet qualified for Professional Membership, and of persons no longer actively engaged in professional work who desire to retain some contact with the field. Student Membership is open only to those graduate or undergraduate students in residence at least half-time who are specializing in meteorology or climatology. Finally, Associate Membership affords anyone who has an interest in the weather the opportunity to become affiliated with the national society.

The *Bulletin* of the American Meteorological Society is its official publication. To cater to the specialist in meteorology, the *Journal of Meteorology* which has won international recognition for

its contributions to scientific thought, publishes the results of original research in meteorology and allied fields. *Weatherwise* serves the interest of amateur weathermen. *Meteorological Monographs* is a series of original contributions of greater length and scope than those contained in the *Journal*. Some of them relate closely to chemistry.

The Society has undertaken the preparation of two publications sponsored by the Air Force Cambridge Research Center. Started in 1950 and published monthly, "*Meteorological Abstracts and Bibliography*" constitute a unique collection of English translations of abstracted publications in every language and include special annotated bibliographies on a wide range of subjects, including some related to chemistry. The "*Compendium of Meteorology*" contains more than 100 articles by leading meteorologists on the present state of knowledge in the field and possible future trends. A new meteorological glossary is in preparation, under contract with the United States Weather Bureau, Department of Defense. The Society is also publishing an impressive volume on Dynamic Meteorology and Weather Forecasting in conjunction with the Carnegie Institution of Washington.

In addition to the national organization, there are local branches of the Society in many cities and areas throughout the world. At least six national meetings are held every year, often including joint sessions with other scientific societies. Awards granted by the Society include the Meisinger Award, designed to stimulate young men to engage in original researches in atmospheric circulation and processes, industrial weather and, and special awards to organizations and individuals who have done outstanding work in meteorology.

The President of the Society is Dr. Robert D. Fletcher, Director of Scientific Services, Air Weather Service, and the Secretary is Professor Henry G. Houghton, Chairman, Department of Meteorology, Massachusetts Institute of Technology. The Executive Secretary's office is located at 3 Joy St., Boston, Mass.

KENNETH C. SPENGLER

AMERICAN PETROLEUM INSTITUTE

The American Petroleum Institute, incorporated in 1919 under the laws of the District of Columbia, is an association of some 10,000 oil men; It is their forum, information bureau, technical clearing house, and national trade association. The objects of the Institute, as stated in its charter, are: (1) to afford a means of cooperation with the government in all matters of national concern; (2) to foster foreign and domestic trade in American petroleum products; (3) to promote, in general, the interests of the petroleum industry in all its branches; (4) to promote the mutual improvement of its members and the study of the arts and sciences connected with the petroleum industry.

The major part of the Institute's work is con-

ducted through its hundreds of working committees and subcommittees, whose membership totals several thousands. In general, the Institute assigns to a working or functional committee no activity unless it previously has been proposed and urged by a group of oil men who are interested in the problem of the subject matter, and unless substantial sentiment for the activity has developed within the industry. If, for instance, a project is approved by the Board of Directors or its Executive Committee, a committee of experts from the oil industry is set up. Once committees and subcommittees have been set up, they remain in existence until there is no longer any need for them and they have been discharged. However, the members of committees must annually be elected or appointed so as to avoid continuance of inactive groups.

The activities of the Institute include the fields of standardization, design, care, and correct practice in the use of equipment; engineering and technology; fundamental research; safety and fire protection; industrial health; product labeling; waste disposal; testing methods and specifications; measuring, sampling, and testing; nomenclature; metallurgy; corrosion prevention; pipeline, highway, waterway, and railroad transportation; radio facilities; fuels and lubricants; agriculture; highways; aviation; vocational and personnel training; education and public relations; finance and accounting; statistics; petroleum reserves; taxation, legislation, and regulation.

D. V. STROOP

AMERICAN POTASH INSTITUTE

The American Potash Institute is a non-profit educational and research organization incorporated under the laws of Delaware, with headquarters in Washington, D. C. It began operations in 1935 and is maintained by five of the leading potash producers in the United States, the American Potash and Chemical Corporation, Duval Sulphur and Potash Company, Potash Company of America, Southwest Potash Corporation, and the United States Potash Company. It concerns itself with problems dealing in a broad way with finding where and how potash can be profitably used in agriculture in the United States, Canada, Cuba and Puerto Rico and Hawaii.

A staff of 16 trained agronomists works with federal, state, provincial and local agricultural research, teaching and extension officials to achieve its purposes. To obtain basic information, some 25 research fellowships and grants are maintained on a rotational basis among the state and provincial agricultural colleges and experiment stations.

An agronomic magazine, *Better Crops with Plant Food*, is issued ten times a year. It is edited primarily for the agricultural advisory and teaching groups and contains articles on the results of investigations on the sound use of plant nutrients in crop production and soil management, written for the most part by the authority who did the work.

A library is maintained which contains over 200,000 books, bulletins, theses and periodicals devoted mostly to soil fertility and crop production. Literature lists and annotated bibliographies are issued for use by research workers.

Deliveries of potash salts by all the leading producers and importers of potash in the United States and Canada are compiled and released to the public quarterly. Prices and indices of crops and of fertilizer materials also are compiled and published.

Branch offices are maintained in Atlanta, Georgia; Lafayette, Indiana; San Jose, California; and Burlington, Ontario

J. D. ROMAINE

AMERICAN SOCIETY OF AGRONOMY

The American Society of Agronomy was founded on December 31, 1907, when a group of professional workers in the field of farm crops and soil improvement met at the Department of Botany of the University of Chicago. Their plan was to organize a professional society for the mutual exchange of ideas in their special field of agricultural research. The meeting followed a call circulated in the fall of 1907 signed by 43 persons interested in agronomic investigations.

The society they founded has grown to include more than 2,600 professional workers in agronomy and soil science, the leading research society of its kind in the world. Although by far the largest number of members are located in the United States, more than fifty foreign countries are now represented on the membership roster.

Objectives of the Society are "to increase and disseminate information concerning crops and soils and the conditions affecting them in order to contribute to the general human welfare." The Society seeks to achieve these objectives by the following means: (1) promoting basic and applied research in farm crops and soils; (2) fostering high standards in crops and soils education and research training; (3) encouraging professional improvement of its active and associate members; (4) making available, both to the public and to workers in related fields, current information on crop and soil science; (5) cooperating with other organizations in the consideration and solution of agricultural problems dealing with farm crops and soils.

Membership in the American Society of Agronomy is open to all individuals and organizations interested in the objectives and program of the Society. Professional agronomists are usually active members of the Society. Commercial men, extension workers, and farm leaders may affiliate either as active members or associate members. Corporations and associations with a special interest in agronomic research may enroll as sustaining members of the Society.

The seven Soil Science Divisions of the American Society of Agronomy have been organized as the Soil Science Society of America since 1936. Meetings of the Soil Science Society of America are held jointly with those of the American Society

of Agronomy each year. Members of the Soil Science Society of America are automatically members of ASA also. The six Crop Science Divisions were formed into the Crop Science Society of America under new by-laws adopted in November 1954. The CSSA has the usual officers and parallels the SSSA in organization and in its relationship to the American Society of Agronomy.

The American Society of Agronomy holds an annual four-day meeting, which attracts upwards of 1,200 members and guests. This meeting is rotated around the country, though it is usually held in a centrally located city. Outstanding research leaders and scientists speak before the general sessions of each annual meeting, and more than forty divisional meetings are held in connection with the specialized fields of farm crops and soil science. At least four regional meetings and one or more special conferences are held annually.

The official organ of the American Society of Agronomy is *Agronomy Journal*, a monthly technical journal devoted to current research reports, including papers presented at the Society's annual meeting. Articles devoted to teaching and extension methods in agronomy are also published. It has about 3,000 subscribers in the United States and seventy-five other countries. The official publication of the SSSA is known as the *Soil Science Society of America Proceedings*. This is a quarterly journal devoted to the latest findings in the field of fundamental and applied soil science. CSSA does not have a separate publication, its members using *Agronomy Journal* as their main outlet for crop science papers.

The Society also publishes *What's New in Crops and Soils*, a nontechnical journal appearing nine times a year, which presents the latest advances in crop and soil improvement in popular form for farm leaders and leading farmers. This publication has a large distribution among the seed, fertilizer, and agricultural chemical industries.

Most of the chemical research conducted by members of the American Society of Agronomy is reported in the Divisions of Soil Chemistry, Soil Microbiology, Soil Fertility, Soil Classification, Crop Physiology and Ecology, and Weed Control. Chemists working with fertilizer materials, soil conditioners, soil amendments, seed protectants, herbicides and similar chemicals will be particularly interested in the publications and activities of the American Society of Agronomy and its several divisions.

L. G. MONTHEY

AMERICAN SOCIETY FOR TESTING MATERIALS

The American Society for Testing Materials was organized in 1898 as the American Section of the International Association for Testing Materials and chartered in 1902 under its present name. It is a nonprofit, technical organization "for the promotion of knowledge of the materials of engineering, and the standardization of specifications and methods of testing." Membership of over 8000 is comprised of corporations and individuals drawn from industry, government and the sciences

and classified into three groups: consumers, producers, and general interest. Its purposes are achieved through activities of some 75 main technical committees and several hundred subcommittees which are responsible for research and the development of standard specifications and methods of test for materials. Some committees have been active for more than 50 years, many in fields related to or importantly concerned with chemistry. Important work has been done in the chemistry of metals, cement, paint, petroleum, synthetics, plastics, cellulose, and others. Within the past five years, committees have been organized on radioactive isotopes, absorption spectroscopy and mass spectrometry.

Almost all the ASTM technical committees have an interest in chemistry of one sort or another and many of them have subcommittees on chemistry, or chemical analysis. Committee E-1 on Methods of Testing has a subcommittee on Correlation of Chemical Analysis. Several main technical committees are assigned fields of activity relating directly to chemistry. Committee E-2 on Emission Spectroscopy was organized in 1932 for the formulation of methods of spectroscopic analysis by emission techniques, including methods of sampling. Important recent publications prepared by this committee are "Symposium on Chemical Analysis of Inorganic Solids by Means of the Mass Spectrometer", "Symposium on Fluorescent X-Ray Spectrographic Analysis", and "Procedures for Emission Spectrochemical Analysis". The last is a volume of 300 pages containing some 50 suggested methods for emission spectrochemical analysis covering a wide range of materials and techniques.

Committee E-3 on Chemical Analysis of Metals was organized in 1935 for the formulation of standard methods of chemical analysis of metals, including methods of sampling and tolerances in values obtained in chemical analysis of metals. "ASTM Methods for Chemical Analysis of Metals" (1950) is a 476-page volume containing some 40 ASTM Standards and Tentatives for recommended practices, sampling methods and methods for chemical analysis of metals. Primarily the work of Committee E-3 it also includes a few methods developed by Committee E-2 when appropriate. A revised edition is scheduled for publication in 1957.

Committee E-13 on Absorption Spectroscopy was organized in 1950 for the coordination and formulation of methods of spectroscopic analysis by absorption, fluorescence, and scattering techniques. This committee has assumed the responsibility connected with the development and maintenance of the punched IBM card system developed by Dr. L. E. Kuenzel of Wyandotte Chemicals Corporation for indexing spectral absorption data. Cards indexing both infrared and ultraviolet spectra are available and are distributed by the American Society for Testing Materials.

Committee E-14 on Mass Spectrometry was organized in 1952 for the promotion of knowledge and advancement of the art of mass spectrometry by: (a) coordinating scientific applications and

methods of analysis based on mass spectrometry, (b) sponsoring meetings at which scientific papers relative to mass spectrometry may be presented and discussed, (c) standardizing nomenclature relating to mass spectrometry, and (d) initiating, sponsoring, and reporting work in the field of mass spectrometry, without prejudice to the jurisdiction of other technical committees over their respective materials. It is the objective of the committee to encourage participation on the widest possible basis of individuals interested in mass spectrometry in order to coordinate and promote the exchange of information in the field. Emphasis is placed on presentation at national meetings of papers on all phases of mass spectrometry with subsequent publication in the most appropriate medium.

A Joint Committee on the Chemical Analysis of Powder Diffraction Methods under the joint auspices of the American Crystallographic Association, the American Society for Testing Materials, the British Institute of Physics, and the National Association of Corrosion Engineers sponsors the development and publication of an X-ray diffraction card file containing data for the identification of materials by the Hanawalt X-Ray Diffraction Method. Cards are available from ASTM either plain (3" x 5") or key sort cards (4" x 6") or on standard IBM punched cards.

The above activities of selected ASTM committees are indicative of the work of the Society in the field of chemistry. As mentioned previously almost all committees have some interest in chemistry as it applies to their work and carry on research activities in their respective fields.

The Society's research activities are carried on through laboratories of industry, colleges, and government. The Society's work is implemented by national, district, and committee meetings and by the publication of a seven-part 11,000-page Book of Standards triennially, with supplements in intervening years; the ASTM *Bulletin*; special technical publications; and special compilations of ASTM Standards. Further information may be obtained from the Society's Headquarters, 1916 Race St., Philadelphia 3, Pa.

F. F. VAN ATTA

AMES LABORATORY

The Ames Laboratory of the Atomic Energy Commission is one of the major Atomic Energy Commission research installations. It is located on the Iowa State College campus on land leased by the Government from the College. It is operated by the Iowa State College, as prime contractor, through the Institute for Atomic Research. The Laboratory specializes in basic and pioneering research in the fields of science underlying the practical application of atomic energy, both for peacetime and military uses. The Laboratory has been particularly successful in being able to produce rare metals, alloys and chemicals which are not available commercially but which the Atomic Energy Commission needs.

The Laboratory employs about 600 people, a

large number of these being part-time employees. Many of the major scientists are employed part-time by the Ames Laboratory and part time by the College on the teaching staff. Many of the younger people are employed half-time in the Laboratory and go to school and work on their theses the remainder of their time. The officers of the Laboratory are: F. H. Spedding, Director, H. A. Wilhelm, Associate Director, A. F. Voigt, Assistant to the Director, C. A. Goetz, Chief, Division of Chemistry, G. W. Fox, Chief, Division of Physics, M. Smutz, Chief, Division of Chemical Engineering.

The Laboratory was organized in 1941 and started early in 1942 under the Office of Scientific Research and Development. It was taken over by the Manhattan District and was one of the four basic laboratories mentioned in Secretary Stimson's report at the end of the war. Since 1946, it has been a major Atomic Energy Commission installation. This Laboratory developed many processes which are now in industrial operation, for example, those for making metallic uranium, metallic thorium, the rare earth elements, etc. During the war this Laboratory produced, on the campus, more than two million pounds of uranium for the early reactors.

Rare Earths. The elements from atomic number 58 to 71, inclusive are known as the rare earths. They are poorly named, since they are neither earths nor rare. They were called rare earths because they were first isolated in the oxide form, and resemble somewhat the common earths Al_2O_3 , MgO , CaO , BaO , etc. Cerium, the most abundant rare earth is reported to be more abundant in the earth's crust than copper, tin, zinc or lead, and even the rarer ones such as terbium and lutetium are more abundant than gold or platinum. In their elemental form they are a group of metals about the color of stainless steel, but considerably softer. In general, they have three electrons in the valence shell or in the conduction bands of the metal. As the charge on the nucleus increases across the series, extra electrons are added to an inner incomplete (4f) shell. For this reason the chemical properties of the rare earths are very similar, and in the past it has been difficult to separate them in the pure form. As the charge on the nucleus increases, the size of the rare earth ion gets progressively smaller (lanthanide contraction) and for this reason, they are a particularly attractive group for research purposes in checking various theories of the liquid and solid state and various theories of chemical reactions, etc.

The elements in column III-A of the Periodic Table (Sc, Y, La and Ac) closely resemble the rare earths in their chemical behavior, and La and Y are always found associated with them in nature. For this reason, these elements are also sometimes called rare earths. The actinide "rare earth" series, elements 90-101, particularly the heavy members, have properties closely resembling the rare earths. Thus it can be seen why the rare earth type elements are so important for theoretical studies, since they represent 30% of the Periodic Table.

The rare earths are found widely scattered in nature in low concentrations, and in high concentrations in certain ores such as bastnasite, monazite, xenotime, gadolinite, fergusonite, euxenite and samarskite. The mixed rare earths have found considerable commercial application as cores for carbon arcs, mischmetal used in the steel industry as a getter, and pyrophoric alloys for cigarette lighters. Lanthanum oxide is used in high quality optical glass, and cerium oxide is widely used as a polishing agent and as a glass opacifier. Whenever uranium, plutonium or thorium fissions, radioactive rare earths compose a fair percentage of the fission products. Some of these have large nuclear cross-sections and have to be removed if the chain reaction is to be maintained. Conversely, these elements could serve as control rods.

In the past, the rare earths were separated by repeated fractional operations, e.g., fractional crystallization, and it required anywhere from a few dozen up to 40,000 fractionations to isolate the individual rare earths in reasonably pure form. Since 1944, the heavier rare earths have been separated rather rapidly by ion-exchange methods, and they are now commercially available, since a number of companies have set up pilot plants for this purpose.

All the rare earths exist in the trivalent state, and samarium, europium and ytterbium exist in the divalent state as well. These latter elements can be readily separated from the others by taking advantage of this lower valency state. Cerium exists in the 4 valent state and can be readily separated from the others by putting it in its oxidized form. Terbium and praseodymium also exist in a higher valent state in the form of the oxide, but aqueous solutions of the high valent form have not yet been prepared.

The metals can be produced by electrolysis in fused halide melts or by thermal reduction of the halides with an active metal such as potassium or, preferably, calcium. Europium, samarium and ytterbium are only reduced to the divalent state with calcium. However, these elements are quite volatile at the melting point and can be readily prepared by heating their oxides with lanthanum metal or mischmetal. The pure samarium, ytterbium or europium can be easily distilled away from the mixture. Most of the rare earth metals are paramagnetic and many of them become anti-ferromagnetic or ferromagnetic at low temperatures.

F. H. SPEDDING

Cross-references: Rare Earths

AMIDES

Amides are organic compounds containing a $-\text{CONH}_2$ group and are closely related to organic acids.

Sodium amide (sodamide) (NaNH_2 , m.p. 210°C) is made by the reaction of metallic sodium with ammonia. If sodium amide is left in contact with air, sodium nitride forms, and the resulting mixture is explosive. Sodium amide reacts with (1) water to form sodium hydroxide and ammonia;

(2) hydrogen to form sodium hydride and ammonia; (3) carbon monoxide to form sodium cyanide, sodium hydroxide, and ammonia; (4) carbon dioxide to form cyanamide (NH_2CN) and sodium hydroxide; (5) carbon disulfide to form sodium thiocyanate and hydrogen sulfide; (6) magnesium to form magnesium nitride; (7) aluminum to form aluminum amide [$\text{Al}(\text{NH}_2)_3$]; (8) alkynes in ether ($\text{RC}\equiv\text{CH} + \text{NaNH}_2 \rightarrow \text{RC}\equiv\text{CNa} + \text{NH}_3$); (9) alkyl halides to form an alkene ($\text{C}_2\text{H}_5\text{I} + \text{NaNH}_2 \rightarrow \text{C}_2\text{H}_4 \uparrow + \text{NaI} + \text{NH}_3 \uparrow$). When heated above 330°C , sodium amide decomposes into its elements. Other alkali amides are known. *Lithium amide* is less reactive than sodium amide. *Potassium amide* is quite similar to sodium amide, but it is much more soluble in liquid ammonia.

Organic amides may be considered to be derivatives of ammonia in which a hydrogen atom has been replaced by an acyl group ($\text{RCO}-$). The simplest amide is *formamide* (HCONH_2 , b.p. 210°C). Amides, like amines, are primary, secondary, or tertiary depending upon the number of hydrogen atoms of ammonia that has been replaced.

Amides may be prepared by (1) rearrangement caused by heating the corresponding ammonium salt ($\text{CH}_3\text{COONH}_4 \rightleftharpoons \text{CH}_3\text{CONH}_2 + \text{H}_2\text{O}$); (2) the reaction between an acid and concentrated ammonia water ($\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{CONH}_2 + \text{C}_2\text{H}_5\text{OH}$); (3) ammonolysis of an acid halide or an acid anhydride by ammonia or by a primary or a secondary amine ($\text{CH}_3\text{COCl} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CONH}_2 + \text{NH}_4\text{Cl}$); (4) partial hydrolysis of a nitrile ($\text{C}_2\text{H}_5\text{CN} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{CONH}_2$).

Amides undergo many reactions. Among them are (1) the formation of salts with strong acids (amides, however, are relatively weak as proton-acceptors); (2) hydrolysis in either acid or alkaline solution. An example of each follows: (1) $\text{CH}_3\text{CONH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{NH}_4^+$; (2) $\text{CH}_3\text{CONH}_2 + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{NH}_3 \uparrow$; (3) reduction essentially by hydrogen to form a primary amine; (4) reaction with nitrous acid to form the corresponding acid, nitrogen, and water; (5) the reaction with an alcohol in the presence of boron trifluoride or hydrochloric acid yields an ester as the chief product; (6) when treated with a strong dehydrating agent such as P_2O_5 or SOCl_2 , water is lost and a nitrile is formed that contains the same number of carbon atoms as the original amide; (7) conversion to a primary amine that contains one fewer carbon atoms than the original amide is accomplished by the Hofman reaction, in which alkaline hypohalite is used.

Acetamide (ethanamide, CH_3CONH_2 , m.p. 81°C) is probably the best known amide. Its colorless crystals are deliquescent. The compound dissolves well in water, glycerol, and ethanol. It lacks odor, and it boils at 222°C . Acetamide is used as a solvent, and in organic syntheses. It is used to make lacquers, explosives, and surface-active agents.

Urea (carbamide, $\text{CO}(\text{NH}_2)_2$, m.p. 132.7°C) is an example of a diamide. Many derivatives of this compound are known. Urea is soluble in water, but it is not generally soluble in most organic sol-

vents. Urea is formed as the end product from the metabolism of protein food. It is excreted in the urine of mammals. Synthetic urea is now manufactured in large quantities by a process in which ammonia and carbon dioxide are carefully heated together under controlled pressure conditions. Synthetic urea is used as an animal-food additive, as a fertilizer, and for the manufacture of resins and plastic materials.

ELBERT C. WEAVER

Cross-references: *Amines, Acids, Ammonia*

AMINES

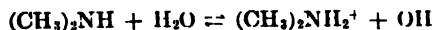
Amines as a group are organic compounds derived from ammonia. Amines are used extensively for a number of purposes: they are solvents, surface-active agents, rust inhibitors in anti-freeze mixtures, and are used to make special soaps employed in the cosmetic and dry-cleaning industries. Amines are intermediates in the synthesis of many useful compounds, some of which become dyes or medicines. Amines also yield salts such as methyl ammonium chloride ($\text{CH}_3\text{NH}_3\text{Cl}$). On extreme alkylation, tertiary amines form quaternary ammonium salts, for example, tetramethyl ammonium chloride [$(\text{CH}_3)_4\text{NCl}$].

Primary amines (RNH_2) such as methyl amine (CH_3NH_2 , b.p. -7°C) have one hydrogen atom of ammonia replaced by an organic radical; secondary amines ($\text{RR}'\text{NH}$) such as dimethyl amine [$(\text{CH}_3)_2\text{NH}$, b.p. 7°C] have two hydrogen atoms of ammonia replaced; and tertiary amines ($\text{R R}'\text{R}''\text{N}$) such as trimethyl amine [$(\text{CH}_3)_3\text{N}$, b.p. 4°C] have no hydrogen attached to nitrogen. These are all alkyl amines. The same three sorts of amines are known with aryl substituents. The simplest primary aryl amine is *aniline* ($\text{C}_6\text{H}_5\text{NH}_2$) or phenyl amine. Mixed amines are also known.

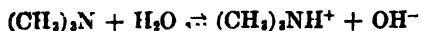
Like ammonia, amines tend to ionize in water and form alkaline solutions. Some of them are even more active than ammonia in this respect. If K is the dissociation constant,



$$K = 2 \times 5 \times 10^{-5}$$



$$5.4 \times 10^{-4}$$



$$5.9 \times 10^{-4}$$

Primary amines may be prepared by (1) reduction of nitro compounds by hydrogen; (2) alkaline hydrolysis of isocyanates or isocyanides; (3) the Hofmann reaction of sodium hypobromite on an amide; (4) action of strong alkali on an amine salt; (5) reaction of an alkyl halide with ammonia; (6) reduction of a nitrile by sodium and alcohol (a special case is the reduction of adipic acid by ammonia, followed by dehydration and then hydrogenation (1,6-hexanediamine [$\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{NH}_2$]

NH_2) forms a compound used in the manufacture of nylon); (7) sodium phthalimide and an alkyl halide followed by alkaline hydrolysis (Gabriel synthesis); (8) reduction of oximes by sodium and alcohol; (9) alcohol vapor and ammonia heated with thorium oxide as a catalyst at 360°C ; (10) from amino acids, as accomplished in the decomposition of fish.

Secondary amines are prepared by (1) alkyl halides reacting with primary amines; (2) the reaction of alkyl halides with sodium cyanamide (Na_2NCN); (3) decomposition of amino acids.

Tertiary amines may be prepared by treating ammonia with an excess of alkyl halide.

Primary amines react (1) with water to form substituted ammonium hydroxide; (2) with acids to form addition compounds; (3) with alkyl halides to form the halides of the corresponding secondary amine; (4) with acid chlorides to form substituted amides (for example, acetyl chloride and ethylamine form *N*-ethylacetamide and ethylamine hydrochloride); (5) with nitrous acid to form a primary alcohol; (6) with chloroform to form the corresponding isocyanide; (7) with Grignard reagents.

Secondary and tertiary amines also react with many of these substances, but the products differ. Mono-, di-, and trimethyl amines are low cost sources of basic organic nitrogen.

Dimethyl amine [$(\text{CH}_3)_2\text{NH}$, sp. gr. 0.68 at 0°C] may be made by the reaction of methanol vapor and ammonia with a catalyst at a high temperature. It is used to unhair hides, to absorb acid gases, as a flotation agent, as a gasoline stabilizer, and as an intermediate in the preparation of local anesthetics and antihistamine, as a rubber curing accelerator, and in electroplating. *Trimethyl amine* [$(\text{CH}_3)_3\text{N}$, sp. gr. 0.662 at -5°C] is used to make choline chloride [$(\text{CH}_3\text{OHCH}_2\text{N}(\text{CH}_3)_3\text{Cl})$], a poultry feed additive.

If a 12- to 24-carbon atom chain is attached to the carbon atom adjacent to the nitrogen atom in a primary amine, the result is a stable liquid that resists oxidation, and which can be used as an oil additive.

A more branched chain amine such as tertiary butyl amine [$\text{CH}_3-(\text{CH}_2)_3-\text{NH}_2$] reacts with aldehydes, cyanogen chloride, and alkyl halides. Uses for the products of these reactions include intermediates for rubber-processing chemicals, insecticides, oil additives, photographic chemicals, dyestuffs, pharmaceuticals, surface active agents, and corrosion inhibitors.

Hexamethylenetetramine [$(\text{CH}_2)_6\text{N}_4$, m.p. 263°C] is made by the combination of formaldehyde and ammonia. It is a sweet-tasting solid, irritating to the skin, and soluble in water. Under the name "Urotropin" or Methenamine, it is used as an urinary antiseptic. It is also used as an accelerator in the curing of rubber, and as a raw material in the manufacture of some plastics. It has a slightly irritating effect on the skin if used regularly.

Other interesting amines include choline, discovered in hog bile and also found in beer; acetyl choline, a medicinal; ethylene diamine, a rubber latex stabilizer and a corrosion inhibitor; and numerous compounds from the decomposition of

proteins such as cadaverine, peptrescin, and neurine.

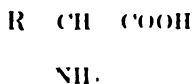
ELBERT C. WEAVER

Cross-references: *Amides, Ammonia, Bases*

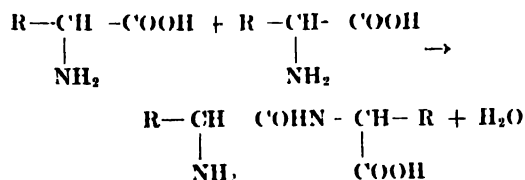
AMINO ACIDS

The amino acids discussed here are strictly the naturally occurring ones. They are the constituents of proteins and should be distinguished from those organic compounds which could fall into this group; for, chemically speaking, the term *amino acid* may be defined as an organic compound that contains in its chemical structure a carboxyl group and an amino or imino group in the alpha position. To avoid confusion it is necessary to set certain conditions for the inclusion of a new amino acid to the list of natural amino acids that have been definitely established as constituents of proteins. These conditions are (1) its isolation and description must have been achieved independently by at least two workers, and (2) its chemical structure must have been established and verified by comparison with a synthetic product either as the racemic or optically active form. These conditions were set by Vickery and Schmidt in 1931 and remain valid.

General Considerations. The natural amino acids are the structural units from which all proteins are synthesized. With the exception of proline and hydroxyproline, their chemical structure may be represented as follows:



In proline and hydroxyproline, the amino group is part of a pyrrolidine ring. Owing to the presence of one or more basic amino and acidic carboxyl groupings in their chemical structures, amino acids have amphoteric properties which permit them to react with acids, with alkalis, or with one another. The manner in which an amino acid reacts with itself, or with another amino acid, is termed condensation (peptide formation) and may be represented as follows:

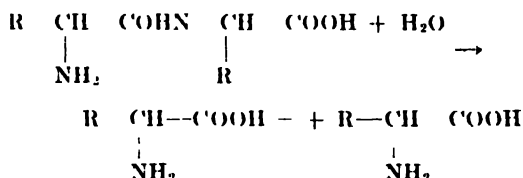


Thus it can be readily seen that on condensing an amino acid with itself or with another amino acid the carboxyl group of one and the amino group of the other are chemically bound to form an amide linkage, with a loss of one molecule of water. This process of condensation may be carried out to form a chain of bound amino acids of indefinite length.

The resultant product of condensing two amino acids is a *dipeptide*, of three amino acids, a *tri-peptide*, of several amino acids a *polypeptide*.

Briefly, one may consider a protein as a polypeptide molecule which consists of a large aggregation of amino acids.

Hydrolysis. The chemical process that involves the breakdown of a protein molecule to its components, the amino acids, is termed *hydrolysis*. Three general agents are employed in the hydrolysis of proteins, viz: (1) *an acid*, such as hydrochloric or sulfuric acid, (2) *an alkali*, such as sodium hydroxide, potassium hydroxide, or barium hydroxide, and (3) a suitable *proteolytic enzyme*. Whatever agent is employed for the hydrolysis of a protein, one molecule of water is gained everytime a peptide bond is broken down. This is illustrated in the following manner:



Therefore it is obvious that whereas through condensation of amino acids one molecule of water is given off for every amide linkage synthesized, one molecule of water is gained on hydrolyzing a peptide linkage and the liberation of two amino acids.

With the exception of glycine, all naturally occurring amino acids are optically active. The synthesis of an amino acid invariably results in an optically inactive form (an equal mixture of D and L). The hydrolysis of proteins by alkalis also yields optically inactive mixture of amino acids. Each optically active amino acid has a specific rotation value which is a characteristic of this particular amino acid. This characteristic is important for identification purposes and nutritionally, as, in most instances, the L-amino acids are metabolized by the animal system.

Amino Acids in Human Nutrition. The term referred to in the literature as an essential, or an indispensable, amino acid has been used interchangeably and has been defined as that amino acid which the animal system cannot synthesize, at least at a rate commensurate with its needs. In the experimental animal, the continued absence of any indispensable amino acid from its diet leads to loss of appetite, loss of weight, characteristic pathologic changes, and eventual death. A dispensable, or nonessential, amino acid is one that the animal system can synthesize. This does not necessarily mean that they are valueless in our dietary requirements.

Rose investigated man's requirements of each of the essential amino acids and determined the minimum requirements of each and made a tentative recommendation of the required daily intakes. A summary of his findings is found in Table I(A).

Lesser-known Amino Acids. In recent years, several amino acids have been isolated from certain proteins. As they occupy a relatively lesser important position in metabolism than the definitely established ones, they have been referred to as "Occasional or Lesser-known Amino Acids".

They are as follows:

Occasional Amino Acids	Sources
Hydroxylysine	Gelatin
Ornithine	Tyrocidine, gramidicine, etc.
Citrulline	Found in the free state—controversial
Octopine	Octopus, scallop muscle
Djenkolic acid	Djenkel nuts and urine
beta Alanine	Pantothenic acid, carnosine, anserine
beta-Thiolvaline	Penicillins
meso-γ ε-Diaminopimelic acid	<i>Corynebacterium diphtheriae</i> <i>Mycobacterium tuberculosis</i>
γ Aminobutyric acid	Bacteria, plants, brain and yeast <i>Corynebacterium diphtheriae</i>
α-γ-Diaminobutyric acid	Polymixins, Circulin
α-Aminobutyric acid	<i>Corynebacterium diphtheriae</i>
α-Amino-γ-guanidinooxy-n butyric acid (canavanine)	Soybeans and Jack beans
α-Amino β,β dimethyl-γ hydroxybutyric acid	<i>Escheria coli</i>
N-Methylisoleucine, N-Methylvaline, an N-Methylleucine	Enniatins
N-Methylimidazole-alanine (methylhistidine)	Urine

Alanine (α-Aminopropionic acid), $[\text{CH}_3-\text{CH}(\text{NH}_2)-\text{COOH}]$. Alanine is the first amino acid obtained by synthesis before it was isolated from the products of the hydrolysis of proteins. It was synthesized by Strecker in 1850. In 1888, Weyl isolated it in the crystalline state from the hydrolyzate of silk fibroin and definitely established its chemical structure.

Silk fibroin is the best source of alanine. The protein is first hydrolyzed with either strong hydrochloric acid or sulfuric acid. From the hydrolyzate, alanine may be conveniently isolated by the classical method of Fischer which consists in condensing the amino acids with ethanol. The resultant product contains a mixture of ethyl esters of the amino acids. It is subjected to fractional distillation *in vacuo* and the fraction that has a b.p. of 50°C at 10 mm pressure consists of alanine-ethyl ester. It is hydrolyzed and pure L-(+)-alanine is obtained. Bergmann and Nieman described another procedure. Glycine is first removed from the acid hydrolyzate of silk as its trioxalatochromate. From the residue, alanine is precipitated with a solution of dioxypyridate.

In 1937, Tobie and Ayres described a satisfactory synthesis which involves the reaction of commercial α-bromopropionic acid with an excess of ammonia. DL-Alanine has also been prepared by the Strecker synthesis. This involves reacting

TABLE I(A). TENTATIVE DATA INDISPENSABLE AMINO ACIDS

Amino Acid	Minimum Daily Requirement gm	Recommended Daily Intake gm	Non-essential Amino Acids
L-Tryptophan	0.25	0.5	Glycine
L-Phenylalanine	1.10	2.2	Alanine
L-Lysine	0.80	1.6	Serine
L Threonine	0.50	1.0	Cystine
L Valine	0.80	1.6	Tyrosine
L Methionine	1.10	2.2	Aspartic acid
L Leucine	1.10	2.2	Glutamic acid
L-Isoleucine	0.70	1.4	Proline
			Hydroxyproline
			Histidine
			Arginine
			Citrulline*

* One of the "occasional" amino acids

TABLE I(B). ESSENTIAL AMINO ACIDS REQUIREMENTS OF THE RAT AND THE CHICK

The amounts given are expressed in grams per 100 grams mixture

Amino Acids	Chick per cent	Rat per cent
Arginine	1.2	*
Glutamic acid	5.0	Not essential
Glycine	1.8	Not essential
Histidine	0.8	0.4
Isoleucine	1.0	0.5
Leucine	1.5	0.8
Lysine	0.9	1.0
Methionine	0.9	0.6
Phenylalanine	1.6	0.7
Threonine	1.3	0.5
Tryptophan	0.5	0.2
Valine	2.2	0.7

* The inclusion of Arginine in the rat's diet accelerates its growth; otherwise, it is not essential.

acetaldehyde with ammonium chloride and sodium cyanide. The resultant hydantoin is hydrolyzed with hydrochloric acid and crude DL-alanine is obtained. The chlorides are removed from the mixture and pure DL-alanine is recrystallized from ethanol.

Alanine is not essential in animal nutrition. It is a constituent of most proteins and occurs to the extent of 25 per cent in silk fibroin.

Arginine. (1-Amino-4-guanidino-*n*-valeric acid), $\text{NH}_2-\text{C}-\text{HN}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)-$
 \parallel
 NH

COOH In 1886, Schulze and Steiger isolated arginine from the aqueous extracts of lupine seedlings. The elucidation of its chemical structure and its isolation in the pure state were accomplished by Hedin in 1895 and in 1910 Sörensen synthesized it.

The protamine salmine contains approximately 85-86 per cent arginine; hence it is the best source

of this amino acid. Arginine is satisfactorily obtained from the acid hydrolyzates of such proteins as hair, fibrin, gelatin, etc., by precipitation with flavionic acid. Arginine flavionate is hydrolyzed with hydrochloric acid and arginine monohydrochloride is crystallized from aqueous ethanol solution.

DL-Arginine is synthesized by reacting cyanamide with benzoylornithine and the resulting product is treated with hydrochloric acid for the removal of the benzoyl group. Pure DL-arginine is obtained by crystallization from ethanol.

Arginine is not an essential amino acid in human nutrition. It is essential to the chick. On basal diets wherein the sole source of protein is replaced by a mixture of all the essential amino acids, rats grow better in the presence than in the absence of arginine. Arginine is readily hydrolyzed by the enzyme arginase, to urea and ornithine. In the avian species, arginine is metabolized to urea and ornithine and the latter is converted to citrulline.

Aspartic Acid (α -Amino-succinic acid), $[\text{HOOC} \cdot \text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}]$. The isolation of this amino acid from asparagine, as a crystalline substance was reported in 1806 by Vauquelin and Robiquet. Some 26 years later, Plisson rediscovered this compound and named it aspartic acid. It was not associated with the constituents of proteins until 1875 when Ritthausen isolated it from the acid hydrolyzates of vegetable proteins and elucidated its chemical structure. Its synthesis was performed by Pictet in 1887.

Aspartic acid is abundant in most vegetable and animal proteins. The best source is asparagine. The latter is digested with acid, and the digest is neutralized with sodium hydroxide to pH 3.0. Then by the addition of two volumes of ethanol, aspartic acid is recovered and recrystallized from water.

DL-Aspartic acid may be synthesized by reacting maleic anhydride and aqueous ammonia in an autoclave at elevated temperature. The solids are treated with HCl; ammonium chloride is removed, and aspartic acid is recovered and recrystallized from ethanol.

Although this amino acid is not essential in human and animal nutrition, it is of considerable interest in metabolism as it plays an important role in transamination mechanism. On deamination by the liver, it is converted to oxalacetic acid which is a very reactive chemical compound. Oxalacetic acid is readily converted to carbohydrate by the liver or used by this organ for detoxication purposes.

Cystine [$\text{Di}(\alpha\text{-Amino-}\beta\text{ thiopropionic acid})$], $[\text{C}_6\text{H}_7\text{N}_2\text{O}_4\text{S}_2]$. In 1810 Wallaston isolated cystine from a urinary calculus. For almost 90 years this sulfur-containing amino acid was not considered a protein constituent until Mörner, and almost simultaneously Embden, isolated it from the acid hydrolyzate of horn. In 1903, Erlenmeyer synthesized this amino acid, and in 1905, Embden elucidated its chemical structure.

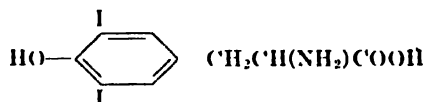
The best sources of L-cystine are hair, horn, and wool. Hair is subjected to acid hydrolysis after having been washed and extracted with cold cleansing solvents. The acid hydrolyzate is then

decolorized with charcoal and neutralized with sodium hydroxide to about pH 4.0. On cooling, crude cystine crystallizes. It is recovered and dissolved in 3N HCl and the mixture is adjusted to about pH 4.0, whereupon crystalline cystine separates out.

The best method for the synthesis of DL-cystine is that of Wood and du Vigneaud. Phthalimido-malonic ester is reacted with benzylthiolmethyl chloride to form S-benzylthiolmethylphthalimido-malonic ester. The latter is hydrolyzed with sodium hydroxide to S-benzylcysteine and the resultant product is treated with sodium in liquid ammonia. DL-Cysteine is obtained and oxidized with ferric chloride to DL-cystine.

Prior to the discovery of methionine, cystine was considered one of the essential amino acids in human and animal nutrition. When the indispensability of methionine was established, cystine was observed to possess a sparing action on dietary methionine. Cystine is a constituent of the tripeptide, glutathione, which plays an important role in tissue oxidation-reduction. Cystine is believed to play an important role in detoxication mechanisms. This sulfur-containing amino acid is abundant in keratogenous proteins, such as wool, hair, finger nails, hooves, and the hormone, insulin.

3,5-Diiodotyrosine (Iodogorgoic acid).



This amino acid was discovered by Drechsel in 1894, who isolated it from the coral "*Gorgonia Carolini*" and termed it iodogorgoic acid. In 1905, Wheeler and Jamieson reported its synthesis.

Diiodotyrosine is found in bath sponges, skeleton of coral (gorgonia) and iodinated proteins and thyroglobulin. It may be prepared by alkaline hydrolysis of sponges. The hydrolyzates are then neutralized with acid and DL-diiodotyrosine is precipitated and recrystallized.

It is conveniently synthesized by treating tyrosine with iodine chloride in acetic acid at a temperature of about 60°C. To the resulting solution, sodium thiosulfate is added to reduce the excess of iodine chloride. Then upon the addition of ammonia, DL-diiodotyrosine is precipitated and recrystallized.

Diiodotyrosine is not essential in human or animal nutrition. However, this amino acid appears to be the precursor of thyroxine, the active principle of the thyroid gland. Through isotopic iodine it has been shown that tyrosine is first converted to diiodotyrosine and the latter finds its way to the thyroid gland where it is converted to thyroxine.

Glutamic Acid (α -Aminoglutaric acid). $[\text{HOOC} \cdot \text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}]$. Glutamic acid was discovered in 1866 by Ritthausen, who obtained it from the acid hydrolyzate of gluten. Wolff synthesized it in 1890 and established its chemical structure.

It is prepared by hydrolyzing gluten with hydro-

chloric acid, decolorizing the acid hydrolyzate with charcoal and concentrating the filtrate. Glutamic acid hydrochloride separates out and is recrystallized and converted to the commercially well-known product, monosodium glutamate.

DL-Glutamic acid may be prepared by reacting methylacrylate, ethylphthalimidomalonate and sodium in absolute ethanol. The mixture is then concentrated and treated with strong hydrochloric acid. After the removal of phthalic acid by filtration and decolorization of the filtrate, the latter is neutralized to about pH 3.0, whereupon *DL*-glutamic acid separates out and is recrystallized.

L-Glutamic acid is not essential in human nutrition but is indispensable to the chick. Glutamic acid has also been reported to be of some value medicinally in the treatment of epilepsy and in the mental development of children. The monosodium salt of glutamic acid has become an important commodity of commerce. Owing to its meat-like flavor, it is being used as a condiment in foods, soups, and sauces. Glutamic acid is very abundant in most vegetable and animal proteins, particularly in wheat gluten and in the residue of beet sugar known as "Steffen's Waste". The latter raw material is the chief source of commercial monosodium glutamate.

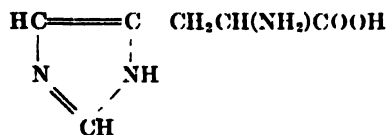
Glycine (α -Amino acetic acid), $[\text{CH}_2(\text{NH}_2)-\text{COOH}]$. Glycine was discovered in 1820 by Braconnot who obtained it from the acid hydrolyzate of gelatin. It was termed glycine by Berzelius, who synthesized it in 1857 and elucidated its chemical structure.

After the removal of glutamic acid from the acid hydrolyzate of gelatin, the residue is brought to dryness and the dry amino acids mixture is esterified with ethanol. Ethylglycine ester is fractionally distilled and promptly converted to its hydrochloride. As the basic ester is unstable, ethylglycine ester hydrochloride is next hydrolyzed with hydrochloric acid and glycine is recovered and recrystallized from ethanol.

Glycine is obtained in good yields by reacting monochloroacetic acid with ammonia. Excess ammonia is removed by distillation and glycine is recovered and recrystallized. As it has no optical activity, synthetic glycine is identical with the natural product.

Glycine is not essential in human and animal nutrition. It is essential to poultry. In metabolism it plays an important role in *in vivo* detoxication of numerous toxic aromatic compounds. It is abundant in most proteins, particularly in gelatin and silk fibroin.

Histidine (α -Amino- β -imidazolepropionic acid).



On April 9, 1896, Kossel isolated this amino acid from the acid hydrolyzate of protamines. He accurately identified its chemical structure and named it histidine. On May 11 of that year, Hedin

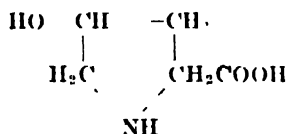
reported its discovery as a protein constituent. The first synthesis of histidine was accomplished by Pyman in 1911.

L-Histidine is obtained by hydrolyzing hemoglobin with hydrochloric acid. The excess HCl is removed preferably *in vacuo* and to the residue 3,4-dichlorobenzenesulfonic acid is added. A precipitate is formed which is recovered and redissolved in hot water. The histidine disulfonate in solution is then treated with barium hydroxide to about neutrality. The insoluble barium sulfonate is removed by filtration. The filtrate is concentrated *in vacuo* and *L*-histidine is crystallized.

The synthesis of *DL*-histidine is rather tedious and the yield is low. Pyman's method has been modified by numerous investigators with moderate improvements. The basic principle involves the reaction of 1-chloromethylimidazole with ethyl acetamidomalonate. The resultant complex product is hydrolyzed to *DL* histidine.

Histidine is essential to animals but not to man. On decarboxylation, it is converted to histamine. This reaction may occur in the intestines as part of the process of bacterial putrefaction. It also occurs in injured or destroyed tissues. *L*-Histidine is a strongly basic amino acid and appears to be a constituent of most well known proteins.

Hydroxyproline (4-Hydroxy-1-pyrrolidine-carboxylic acid).



This amino acid was discovered by Fischer in 1902 among the acid hydrolyzate of gelatin. In 1905 Leuchs synthesized it, elucidated its chemical structure, and termed it hydroxyproline.

The hydrolyzate of gelatin is first treated with flavionic acid to remove arginine. Proline is next removed from the filtrate as is rhodanilate salt and the hydroxyproline is then precipitated as the reineckate. By treatment of hydroxyproline reineckate with pyridine the pure amino acid is freed from its salt, recovered, and recrystallized.

DL-Hydroxyproline is obtained by first reacting acetoacetic ester with epichlorhydrin and converting the resulting product to the oxime by the action of nitrosyl sulfuric acid. This is followed by reduction with hydrogen using platinum oxide as a catalyst and treatment of the reduced product with ammonia. *DL*-Hydroxyproline is then separated from the allo isomers via its copper salt.

This amino acid is not essential in human or animal nutrition. Little is known about its metabolism. Ingestion of hydroxyproline has been reported to give rise to glucose in the experimental animal. Gelatin and hemoglobin are the best sources.

Isoleucine (α -Amino- β -methyl-*n*-valeric acid), $\left[\begin{array}{c} \text{H}_2\text{C} \\ \diagdown \quad \diagup \\ \text{CH}-\text{CH}(\text{NH}_2)\text{COOH} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C}_2 \end{array} \right]$. This amino acid

was discovered by Felix Ehrlich in 1903. Bouveault and Loequin synthesized it in 1906.

Isoleucine and its isomer, leucine, are simultaneously precipitated as their copper salts from de-sugared beet syrup. The two salts are separated by fractional crystallization from methanol. L-Isoleucine is very difficult to isolate in a pure form entirely free from methionine and leucine.

DL-Isoleucine may be prepared by bromination of α -bromo- β -methylvaleric acid. The corresponding α bromo acid is then treated with ammonia. On repeated fractional recrystallization from 80 per cent methanol DL-isoleucine is freed from allo-isoleucine.

L-Isoleucine is an essential amino acid in human and animal nutrition. It appears to be abundant as a component of most dietary proteins. The best source of L-isoleucine is the residue of beet sugar (Steffen's Waste).

Leucine (α -Aminoisocaproic acid), $[(CH_3)_2CH-CH_2CH(NH_2)COOH]$ This amino acid was discovered by Proust in 1819 who isolated it in a crude form from cheese by-products. Subsequently Braconnot obtained it in the crystalline state from the hydrolyzates of muscle and wool proteins, and named it leucine. The elucidation of its chemical structure was accomplished by Schulze and Fikernik in 1891, and its synthesis by Erlenmeyer, Jr. and subsequently by others.

Leucine is obtained by hydrolyzing casein or hemoglobin in sulfuric acid. The sulfate ions are removed with barium hydroxide while the mixture is hot. The clear filtrate is decolorized with charcoal and allowed to cool. Tyrosine separates out and is removed by filtration. The filtrate is concentrated *in vacuo*, acidified with hydrochloric acid and heated. Sodium-2-bromotoluene 5-sulfonate is added to precipitate leucine. The precipitate is recovered, treated with barium chloride and leucine is recovered from the filtrate, and recrystallized by dissolving it in hot water and ammonium hydroxide. Ammonia is removed by evaporation. L-Leucine is thus obtained in a pure state.

Isocaproic acid is converted to α -bromoisocaproic acid by bromination. The bromo compound is treated with ammonia. DL-Leucine is recovered and recrystallized from 50 per cent ethanol.

L-Leucine is an essential amino acid in human and animal nutrition. It appears to be abundant as a constituent of most dietary proteins.

Lysine (α - ϵ -Diamino-*n*-caproic acid), $[H_2NCH_2CH_2CH_2CH_2CH(NH_2)COOH]$. This amino acid was discovered by Drechsel in 1889. The elucidation of the chemical structure and synthesis of lysine were accomplished by Fischer and Weigert in 1902.

L-Lysine is usually obtained as its monohydrochloride salt. Blood corpuscles are hydrolyzed with sulfuric acid and the sulfate ions are removed with barium hydroxide. The filtrate is decolorized with charcoal and picric acid is added to the filtrate. The recovered lysine picrate is digested with hydrochloric acid. Picric acid is removed by filtration, and L-lysine is then crystallized as its monohydrochloride salt.

DL-Lysine may be prepared from cyclohexanone by converting it to cyclohexanoneoxime. The latter is carefully treated with sulfuric acid and reacted with benzoyl chloride to yield benzoyl-aminocaproic acid which is converted to the α -bromo acid and treated with ammonia. On suspending benzoyllysine in hydrochloric acid and refluxing the mixture, benzoic acid separates out and DL-lysine is then recovered as its monohydrochloride salt and recrystallized.

L-Lysine is an essential amino acid in human and animal nutrition. Cereals in general, such as wheat, rice, corn, oats, barley, etc., and the corresponding food products such as flour, gluten, corn meal, zein, rice flour, cottonseed, cottonseed flour, etc., are deficient in lysine. By supplementation with L-lysine, the nutritive value of these vegetable proteins is considerably enhanced.

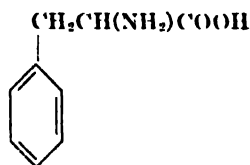
Methionine (α -Amino γ -methylthio-*n*-butyric acid), $[CH_3S-CH_2CH_2CH(NH_2)COOH]$. This sulfur containing amino acid was discovered by Mueller in 1921. Barger and Coyne synthesized it in 1928, identified its chemical structure, and, after consultation with Mueller, named it methionine.

It is prepared by treating the acid hydrolyzate of casein with mercuric sulfate. Methionine, tryptophan, and some tyrosine are precipitated. The precipitate is suspended in water and mercury is removed as its sulfide. Tryptophan and methionine are then subjected to fractional crystallization. L-Methionine is finally obtained in very small yields.

Numerous methods have been devised for the synthesis of DL-methionine. One of these consists in reacting acrolein with methylmercaptan and treating the resulting product with HCN to form γ -methyl-thiolpropionaldehyde cyanohydrin. The latter is then reacted with ammonia under pressure to obtain γ -methylthiolbutyronitrile. Upon hydrolysis of the latter compound with sulfuric acid and neutralization with lime, DL-methionine is obtained and recrystallized.

Methionine plays several important roles in metabolism: (1) It is essential in human and animal nutrition. (2) By virtue of its sulfur content, it is the source of dietary organic sulfur in the body. (3) Owing to its labile methyl group, it is of importance in transmethylation mechanism in the *in vivo* synthesis of choline, creatine, and phospholipides. (4) It has also been reported useful in detoxication of certain poisons. Because numerous foodstuffs of vegetable sources are deficient in methionine, most chicken feed is supplemented with it to the extent of 0.1 per cent. It is also incorporated in certain medicinal products.

Phenylalanine (α -Amino- β -phenylpropionic acid).



This amino acid was discovered by Schulze and

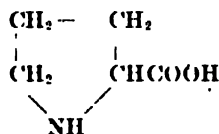
Barbieri in 1879 who isolated it from the sprouts of lupine. It was synthesized by Erlenmeyer and Lipp in 1883, who elucidated its chemical structure and named it phenylalanine.

L-Phenylalanine is difficult to isolate in a pure state. It is obtained from the acid hydrolyzate of hemoglobin from which L-leucine has been removed. The leucine-free filtrate is treated with 2,5-dibromobenzenesulfonic acid and the mixture is refrigerated. L-Phenylalanine 2,5-dibromobenzenesulfonate separates out, is removed by filtration, recrystallized, and the crystalline product is treated with pyridine. Crude L-phenylalanine is recovered, dissolved in hot water-alcohol mixture. Dilute ammonia is added and L-phenylalanine is obtained.

DL-Phenylalanine is easily prepared by bromination of phenylpropionic acid and treating the resulting bromo product with ammonia to yield DL-phenylalanine.

L-Phenylalanine is essential in human and animal nutrition. It is abundant as a constituent of most dietary proteins. In the animal system, phenylalanine is easily converted to tyrosine but the reverse is not true. Apparently this amino acid is an important intermediate from which the adrenal glands synthesize epinephrine and arterenol via its conversion to: tyrosine, dihydroxyphenylalanine, decarboxylation and conversion to arterenol. The methylation of arterenol yields epinephrine.

Proline (α -Pyrrolidinecarboxylic acid).



This amino acid was synthesized in 1900 by Willstätter. It was not established as a component of proteins until a year later when Fischer isolated it from the acid hydrolyzate of gelatin via its ester.

After the removal of arginine from the acid hydrolyzate of gelatin with flavonic acid, a methanol solution of ammonium rhodanilate is added to the filtrate. The mixture is cooled and proline rhodanilate is recovered and recrystallized from an acidified alcoholic solution. Rhodanilic acid is removed by treatment of the crystalline product with pyridine. L-Proline is obtained.

DL-Proline may be synthesized by condensing sodium malonic ester with trimethylene bromide. The resulting product is then brominated in the cold to yield dibromopropylmalonic ester. The latter compound is treated with ammonia in the presence of methanol and saponified with barium hydroxide to obtain DL-proline.

Proline is not essential in human and animal nutrition. It is a constituent of most proteins. Apparently it does not play any specific role in metabolism.

Serine (α -Amino- β -hydroxypropionic acid), $[\text{CH}_2(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}]$. This amino acid was discovered by Cramer in 1865. Owing to the difficulty of its isolation from protein hydrolyzates,

it remained in complete oblivion for the following 30 years. Its synthesis was accomplished in 1902 by Fischer and Leuchs.

L-Serine is prepared from the sulfuric acid hydrolyzate of silk fibroin. The sulfate ions are removed as barium sulfate and the filtrate is decolorized with charcoal and concentrated *in vacuo*. Tyrosine separates out and is removed. Glycine is next recovered from the filtrate as 5-nitronaphthalene-1-sulfonate. The glycine-free filtrate is treated with azobenzene-p-sulfonic acid to precipitate out alanine. The clear filtrate obtained after the removal of alanine is treated with p-hydroxyazobenzene-p'-sulfonic acid. The serine hydroxyazobenzene sulfonate separates out, is recovered, and suspended in hot water, and barium acetate is added to remove the sulfonic acid. The filtrate is heated, decolorized with charcoal, and concentrated *in vacuo*. Crude L-serine is recrystallized from 80 per cent ethanol.

Methyl- α -bromo- β -methoxypropionate is treated with methanol in the presence of mercuric acetate. The resulting product is brominated and the bromo compound is heated with sodium hydroxide and subsequently neutralized with sulfuric acid. The mixture is brought to dryness and α -bromo- β -hydroxypropionic acid is converted to DL-serine by treatment with ammonia. Crude DL-serine is recovered and crystallized from ethanol.

Although L-serine is not essential in human and animal nutrition, its presence in the diet has been reported to enhance the biosynthesis of cystine from methionine.

Threonine (α -Amino- β hydroxy-*n*-butyric acid), $[\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}]$. In 1930, Rose discovered, elucidated the chemical structure, and named this amino acid, threonine. Its synthesis was accomplished by Carter in 1935.

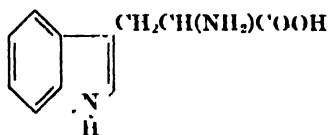
The isolation of L-threonine in a pure state is very difficult. It may be prepared from the sulfuric acid hydrolyzate of casein. The sulfate ions are removed by barium hydroxide and the clear filtrate is concentrated *in vacuo*. Tyrosine and a considerable portion of leucine, isoleucine, and phenylalanine crystallize out and are removed by filtration. Cupric carbonate is added to the concentrated filtrate and the insoluble copper salts of certain other amino acids are removed. Copper is removed from the filtrate as CuS . The copper-free filtrate is concentrated *in vacuo* and extracted with butanol. The water-soluble fraction is freed from its butanol, brought to dryness *in vacuo*, dissolved in water and treated with sulfuric acid and phosphotungstic acid. The mixture is filtered and the excess phosphotungstic acid and sulfuric acid is removed with barium. The residue contains crude threonine. Repeated crystallizations of the crude product yields crystalline L-threonine.

DL-Threonine may be prepared by reacting crotonic acid with methanol and mercuric acetate. The addition product obtained is dissolved in a solution of potassium bromide and bromine is added. Excess bromine is destroyed with sodium bisulfite and the mixture is acidified with HBr and extracted with ether. The α -bromo- β -methoxy-*n*-butyric acid is aminated under pressure

and concentrated *in vacuo*. The resulting product is treated with formic acid, then with acetic anhydride. Formyl-DL-*o*-methylallo-threonine is obtained and refluxed with HBr, concentrated and the residue is neutralized with ammonia and crystallized from ethanol. DL-Threonine is thus obtained and recrystallized from ethanol.

L-Threonine is of considerable biochemical interest. Prior to its discovery by Rose in 1930, no investigator was capable of maintaining life in the experimental animal on a basal diet in which a mixture of pure amino acids was the sole source of nitrogen. Since, it has been shown to be an essential amino acid to all laboratory animals investigated and to man. It is a component of most dietary proteins.

Tryptophan (α -Amino- β -indolepropionic acid).



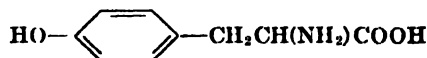
It was discovered, identified, and named by Hopkins and Cole in 1902, and in 1907 Ellinger and Flammann reported its synthesis.

Casam is digested with trypsin and the enzymatic digest is slightly acidified with sulfuric acid and filtered. The filtrate is concentrated *in vacuo* until most of the tyrosine has crystallized. Tyrosine is removed and the clear filtrate is treated with a solution of mercuric sulfate and sulfuric acid. The mercury salt of tryptophan is recovered and mercury is removed as its sulfide. The mercury-free filtrate is concentrated *in vacuo* and extracted with butanol. The butanol fraction is concentrated *in vacuo* and the residue is refrigerated. Crude L-tryptophan is recovered and recrystallized from ethanol.

Several methods have been devised for the synthesis of this amino acid. (1) Condensation of indolealdehyde with hippuric acid gives a low yield of DL-tryptophan. (2) Conversion of indolealdehyde to the corresponding hydantoin and alkaline hydrolysis of the resultant product yields DL-tryptophan. (3) Ethyl acetamidocyanacetate is alkylated with gramine (3-dimethylaminomethyl-indole) and alkaline hydrolysis of the resultant product reportedly gives a high yield of DL-tryptophan.

Many proteins of vegetable origin are deficient, or devoid, of tryptophan which has been shown to be an essential amino acid in human and animal nutrition. This important component of proteins was most illusive to the scientists of the 19th century, as every attempt made to isolate and identify it failed. The main reason for this was that researchers in this field relied on the procedure of acid hydrolysis of proteins which destroyed this amino acid. Tryptophan, on the contrary, is unusually stable to the action of strong acids, provided it is free from traces of impurities containing either aldehyde or ketone radicals.

Tyrosine (α -Amino- β -hydroxyphenylpropionic acid).



In 1846 Liebig discovered this amino acid and named it tyrosine. In 1849, Bopp, in Liebig's laboratory, discovered the method of hydrolysis of proteins with hydrochloric acid and effected the separation of tyrosine from leucine by glacial acetic acid. The latter dissolves leucine but not tyrosine. Erlenmeyer and Lipp synthesized tyrosine in 1883.

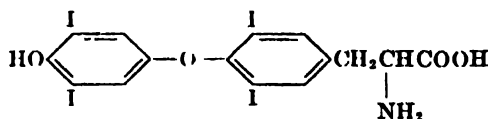
L-Tyrosine is readily prepared from the acid or from the enzymatic digests of proteins such as casein. After the removal of the hydrochloride or sulfate ions from the digest, the filtrate is concentrated and cooled. Crude tyrosine separates out. It is recovered, dissolved in dilute hydrochloric acid, decolorized with charcoal and the clear filtrate is neutralized with ammonia. Tyrosine crystallizes on cooling.

DL-Tyrosine may be prepared by condensing anisaldehyde and hippuric acid in the presence of acetic anhydride and sodium acetate. The resulting product is refluxed in alcoholic sodium hydroxide and neutralized with sulfuric acid. DL-Tyrosine is recovered and crystallized from aqueous ethanol.

L-Tyrosine, a constituent of most proteins, is not essential in human and animal nutrition, but its presence in the diet may reduce the phenylalanine requirements. This amino acid has been studied extensively owing to its close chemical relationship to epinephrine, to thyroxine, and to skin pigmentation. The latter phenomenon is attributed to tyrosine being the immediate source of melanin. On decarboxylation of tyrosine, tyramine is formed.

In acute yellow atrophy of the liver and in certain diseases involving pathologic changes of this organ, tyrosine is apparently not deaminated, hence excreted unchanged. This metabolic disorder is known as tyrosinuria.

Thyroxine [α -Amino- β -(3,5-diiodo-4-(3',5'-diiodo 4'-hydroxyphenoxy)phenyl) propionic acid]



Thyroxine is the chief active principle of the thyroid gland. Kendall was the first to isolate it in a crystalline form. The synthesis and elucidation of its chemical structure were accomplished by Harrington and Barger in 1927.

Dehydrated thyroid glands are digested with alkalis and not with acids. On neutralization of the digest, an iodine-rich fraction precipitates out. This is recovered. The filtrate is collected and concentrated. Another insoluble fraction separates out which is also rich in iodine. This process is repeated several times. The several iodine-rich fractions are combined and dialyzed. The non-dialyzable fraction is dissolved in alcohol, filtered

and brought to dryness *in vacuo*. Crude DL-thyroxine is obtained. This is recrystallized several times.

Thyroxine is now obtained by the iodination of casein, removal of excess iodine and hydrolyzing the iodinated casein with sodium hydroxide. The following steps are almost identical with those described in the preceding paragraph. The thyroxine obtained by alkaline hydrolysis of thyroid glands or iodinated casein is optically inactive as it is racemized during alkaline hydrolysis.

The synthesis of DL-thyroxine is very tedious and the yield is poor. It may be prepared by reacting quinol monomethylether with 3,4,5-triodonitrobenzene. The nitro group of the resulting product is reduced to the amine and converted to the nitrile and then to the aldehyde. Via the azlactone synthesis α -benzoylamino 3,5 diiodo-4-(4'-methoxyphenoxy)cinnamic acid is obtained and converted to α -amino β -(3,5 diiodo 4 (1'-methoxyphenoxy)phenyl)propionic acid. On iodination of the latter DL-thyroxine is obtained.

L-Thyroxine is the active, physiological principle of the thyroid gland. A deficiency of thyroxine results in the development of goiter and a decrease in metabolic processes.

Valine (α -Aminoisovaleric acid), $[(CH_3)_2CH \cdot CH(NH_2)COOH]$. Valine was discovered in 1856 by von Gorup-Besanez and synthesized in 1878 by Schmidt and Sachtlaun. The elucidation of its chemical structure was accomplished by Emil Fischer, who also resolved the racemic DL-valine.

The best starting materials for the isolation of L-valine are lupine sprouts and other similar plant sprouts. After the removal of asparagine, leucine, and proteins from the extracts of plant sprouts, the filtrate is concentrated and phenylalanine and valine are recovered from the residue. These two amino acids are converted to their respective copper salts and separated by fractional crystallization.

DL-Valine may be synthesized by bromination of isovaleric acid and treating the resulting α -bromoisovaleric acid with ammonia. The crude ammonia-free product is decolorized and DL-valine is crystallized from 50 per cent ethanol.

L-Valine is a constituent of most dietary proteins. Despite the simplicity of its chemical structure, it is an essential amino acid in human and animal nutrition. The omission of valine from the diet of the rat gives rise to most unusual physiologic disorders, as besides loss of appetite and loss of weight, the valine deficient animal loses all sense of coordination and becomes very sensitive to sound. Its continued absence from the diet results in eventual death of the animal. In man, a deficiency of valine results promptly in a negative nitrogen balance.

MELVILLE SAIYUN

Cross-references: *Proteins, Nutrition, Polypeptides*

AMINOPLAST RESINS

Some organic compounds possessing free amino ($-NH_2$) groups or functions can form addition compounds with formaldehyde called 'methylol'

compounds, for example,



These methylol compounds can react further by a variety of mechanisms; for example, the following have been suggested:

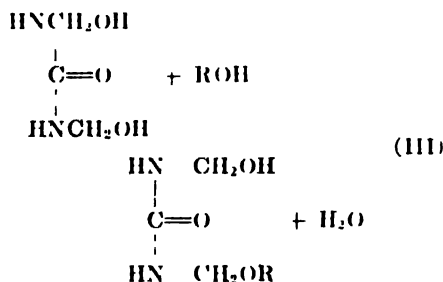


or



If amino compounds are used which have more than one amino group per molecule, polymethylol compounds can be formed. Although existence of tri- or tetramethylol urea is disputed, it seems possible to obtain all variations with melamine from mono- to hexamethylol melamines.

Other substituted ureas, thioureas and substituted triazene, aniline and other formaldehyde reactive compounds can be used alone or in mixtures to obtain the methylol compounds, which can be considered to be the basic monomers of aminoplast resins. The methylol hydroxyls readily form ethers with alcohols, and the presence of an alcohol, such as butanol, in the reaction mixture effectively restricts the reactivity of methylol groups with each other (or with amino hydrogens) by reducing the methylol functionality of the polyfunctional methylol monomer, for example,



These alkylated methylol compounds can condense to form larger molecules before gelation ensues; that is, higher molecular weight compounds can be produced which nevertheless remain more soluble in the solvents used in the reaction medium because molecular weight is achieved more by linear propagation than by extensive branching or crosslinking. Nearly all solution resins used in paint formulation are prepared in this manner, where cross-linking possibilities of the resin at low molecular weight are restricted by etherifying the monomer partly with butanol or other alcohols. Without this chemical modification with alcohol, very low molecular weight water- or alcohol-soluble resins can be prepared. These are used ordinarily as adhesives or in molding compounds, but rarely as coatings resins.

Even alkylated resins are poor film formers unless they are blended with other resins. At high temperatures the unmodified aminoplast enters into extensive polymerization reactions leading to a high degree of branching and cross-linking. Even alkylated resins suffer a reversal of the blocking

reaction (III) at high temperatures, thereby increasing their possibilities for polymerization reactions. If another material of low volatility is present which contains free hydroxyl groups (such as an alkyd or polyester resin) an exchange reaction can take place which liberates butanol and forms a covalent bond joining dissimilar resinous molecules. Such hybridization seems to occur between butylated melamine and phenolic resins (clear coatings for brass), between urea or melamine resins and alkyd resins (automotive or white appliance finishes), and between epoxy resins and any of the amino resins. In the last example, it is probable that the reaction is more complicated than can be explained by ether exchange. In all these instances a more flexible and more adherent film is obtained than when the aminoplast resin is the sole film-former.

The curing of aminoplast resins produces a considerable volume of volatiles, such as water, alcohol, formaldehyde and sometimes other decomposition products. In particular, this feature complicates design of molding dies (which must have provision for "breathing"). In adhesives and paints, curing conditions must be such that expulsion of volatiles is sufficiently slow to prevent blistering and other film defects, caused by the disruptive effects of vapors being expelled from viscous films.

Aminoplast resins are competitive with phenolic resins in many applications. Principally they possess the advantage of better whiteness retention during cure and also during subsequent aging of the plastic or film. This color retention feature has been valued particularly in the production of objects like molded housings for grocery scales, plastic dinnerware, white appliance coatings, and light-colored plywood. In most uses aminoplasts fulfill a role which phenoplasts cannot serve because of their inferior resistance to darkening.

Compared to phenoplasts of equal durability, aminoplast resins are more costly. In coatings applications this feature is compensated by the fact that small proportions of aminoplasts (5-35% by weight) mixed with alkyd resins produce films which are upgraded in hardness, chemical resistance, color retention and in speed of cure at baking temperatures. Such combinations of alkyd and aminoplasts provide the major class of vehicles used to formulate baking finishes for industrial goods like automobiles, machinery, home appliances, venetian blinds, and in general, for most metal goods painted on high-speed production lines. This represents one of the more important uses of aminoplast resins. Other large-scale uses are in decorative laminates, e.g., brightly colored counter and table tops. In molding of plastic items, the commercial possibilities are numerous; however, the volume used today is restricted by the high materials cost of aminoplast resin types. The higher cost compared to phenoplasts seems to be justified only where the greater decorative properties coming from improved color retention are desired along with superior durability.

WILLIAM VON FISCHER AND EDWARD G. BOBALEK
Cross-references: *Plastics, Alkyd Resins*

AMMINES, *see* CHELATION

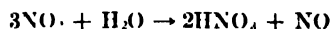
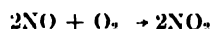
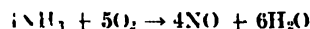
AMMONIA

Ammonia is a colorless alkaline gas (NH_3 , m.w. 17.03) at one atmosphere with a penetrating odor, lighter than air. The word is derived from sal ammoniac (ammonium chloride), said to have been first obtained from camel's dung near the temple of Jupiter Ammon in Egypt. It is formed by destructive distillation of hartshorn (hoofs, horn) (Spirits of hartshorn).

Physical Properties. B.P. -33.35°C ; F.P. -77.7°C ; critical temperature 133.0°C ; critical pressure 1657 psi. Specific heat at constant pressure for pressure of one atmosphere: 0°C 0.5009 cal/g, at 100°C 0.5317; at 200°C 0.5029. Heat of formation, near 0°K , 10,329 cal/mole; 700-1000 $^\circ\text{C}$ 12,000-12,800 cal/mole. Solubility in water at one atmosphere, NH_3 , % by weight: 0°C 42.8, 20°C 33.1, 40°C 23.4, 60°C 14.1. On compressing and cooling NH_3 condenses to a liquid approximately 60% as heavy as water. Because of the high vapor pressure of the liquid at room temperature, it is shipped in pressure cylinders.

Chemical Properties. *Oxidation reactions.* Ammonia does not support ordinary combustion but it does burn with a yellow flame in air or oxygen (ignition temperature 780°C): $4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$. An ammonia and air mixture will explode under certain conditions; high temperature and pressure greater than atmospheric. Ammonia is also oxidized by many oxides: $3\text{CuO} + 2\text{NH}_3 \rightarrow 3\text{Cu} + \text{N}_2 + 3\text{H}_2\text{O}$.

Under the proper conditions ammonia may be oxidized to nitric acid (platinum gauze catalyst):



In general reducing agents do not affect NH_3 . Ammonia is stable at ordinary temperatures but it decomposes into nitrogen and hydrogen at 150-500 $^\circ\text{C}$ under atmospheric pressure. In the presence of catalysts this decomposition may take place at 300°C .

Liquid ammonia is an important ionizing solvent (dielectric constant equal to 16.9 at 25°C) which has been used in many electrolytic solution investigations. Sodium and potassium dissolve in liquid ammonia to form highly conducting colored solutions. Potassium dissolves slowly forming the amide: $2\text{K} + 2\text{NH}_3 \rightarrow 2\text{KNH}_2 + \text{H}_2$. Chlorine, bromine, and iodine all react.



Phosphorus reacts with ammonia at red heat to form phosphine and nitrogen: $2\text{NH}_3 + 2\text{P} \rightarrow 2\text{PH}_3 + \text{N}_2$. Sulfur vapor reacts with ammonia to form ammonium sulfide and nitrogen.

Ammonia forms a great variety of addition compounds which are often called ammoniates in analogy with hydrates.

The water solution of ammonia is distinctly alkaline. The reaction between water and am-

monia may be represented by:



If an aqueous solution of NH_3 is neutralized with an acid, nitric (HNO_3) hydrochloric (HCl), or sulfuric (H_2SO_4), the corresponding salt is formed: NH_4NO_3 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$. The radical NH_4 is referred to as the ammonium radical.

NH_3 forms many coordination compounds, which are often called amines, e.g., $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$.

The double decomposition in which NH_3 is a reactant is known as ammonolysis in analogy with hydrolysis. The substitution of an $-\text{NH}_2$ (amine) group for Cl , OH , SO_3H , is known as amination by ammonolysis.

Production. Ammonia is one of the by-products in the coking of coal. About 5.5 to 6.5 lbs. of ammonia per ton of coal coked is recoverable as ammonia. Dobereiner was the first to synthesize ammonia from nitrogen and hydrogen. Le Chatelier was the first to recognize that to produce ammonia commercially high pressure was needed. Haber studied the thermodynamics of the nitrogen-hydrogen equilibrium. Lewis and Randall calculated the change of free energy, and the change of specific heat for the equilibrium as a function of temperature.

The process used to produce the largest quantity of ammonia today is the Haber-Bosch process, which consists essentially of the following: water gas (CO , H_2 , CO_2) is made from coke, air, steam. The mixed gas (which also contains N_2) passes through a scrubber cooler where dust particles and undecomposed material are removed with water. Most of the CO is converted to CO_2 and removed with a carbon dioxide purifier. The rest of the CO is removed with an ammoniacal cuprous solution. The pure gases (3H_2 to N_2) pass over a catalyst in a high pressure (of the order of 100 atm) and high temperature (near 1000°K) ammonia converter. The ammonia generated is absorbed and removed by water. Modifications of this process are used widely. The modifications consist of differences in sources of the N_2 and H_2 , the methods of purifying the catalysts, the temperature and pressure and the methods of ammonia recovery.

Storage. Anhydrous ammonia is usually stored at pressures up to 40 psi. Cylinders containing up to 150 pounds and 26 ton tank cars are usually used for shipping it. Anhydrous ammonia is marketed under two specifications: (1) commercial grade—ammonia content not less than 99.5%, (2) refrigeration grade 99.95% NH_3 . The nonbasic gas content is not less than 0.20 ml/gm NH_3 , moisture content less than 0.01 ml per 100 ml NH_3 , pyridine content none.

Toxicology. There are four hazards connected with ammonia: (1) pressure, (2) thermal, (3) physiological, (4) explosive. Solutions of ammonia are much less dangerous to handle than the pure substance. There is no pressure hazard; the physiological hazard is eliminated. Liquid ammonia severely irritates the skin. Gaseous ammonia intensely irritates moist tissue. High concentrations of ammonia cause cessation of respiration.

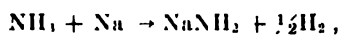
Uses. Ammonia is oxidized in great quantities to make nitric acid, which is used to make TNT, nitroglycerine, nitrocellulose, and ammonium nitrate. In the textile industry ammonia is used in the production of synthetic fibers, e.g., nylon, cuprammonium rayon. Ammonia is also used in the dyeing and scouring of cotton, wool, rayon and silk. The principal nitrogen carriers in fertilizers are anhydrous ammonia, ammonium nitrate, urea, and calcium cyanamide. Anhydrous ammonia is also used to ammoniate superphosphates in the preparation of mixed fertilizers.

Ammonia is used as a catalyst in the phenol-formaldehyde (Bakelite) condensation and also in the urea-formaldehyde condensation to make synthetic resin. The melamine component of melamine-formaldehyde resins are produced by the polymerization of diacyanodiamide in the presence of ammonia. The sulfa drugs, sulfanilimide and sulfapyridine, as well as many vitamins and antimalarials, use ammonia in their synthesis. In the petroleum industry, ammonia is used as a neutralizing agent to prevent corrosion due to acidic components in the petroleum products. In the rubber industry, ammonia is added to raw latex to prevent coagulation during transport from plantation to factory.

Ammonia is the most commonly used refrigerant to produce ice, to air condition, for cold storage. Its characteristics of high latent heat of vaporization, low density, high stability and low corrosion make it valuable in this respect.

A recent development is the substitution of NH_3 for Ca in the bisulfate process for pulping wood. This improves the yield and quality of the pulp. NH_3 is also used as a solvent for casein in the coating of paper.

Chemicals. Ammonium salts are produced in the inorganic chemical field by the neutralization of ammonia with an acid. The following equation represents the production of sodium cyanide:

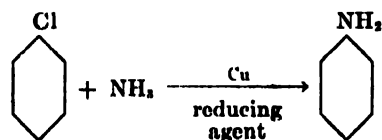


sodium amide



The nitric oxide required for the conversion of sulfur dioxide to sulfur trioxide in sulfuric acid manufacture is obtained from the oxidation of ammonia. The bulk of nitric acid used in the United States is obtained from ammonia oxidation. The Solvay ammonia-soda process for the production of soda ash from sodium chloride uses large quantities of ammonia.

In the organic chemical field amines, amides, nitriles are produced with ammonia, e.g., aniline:



Metallurgy. Ammonia is a processing agent to recover copper, molybdenum, and nickel from ores. Anhydrous ammonia, after it has been dis-

sociated into N_2 and H_2 , is used in nitriding alloy sheets to impart a hard wearing surface. In powder metallurgy, ammonia is used as a protective atmosphere in sintering operations. Metal oxides are reduced with ammonia gas in atomic H_2 welding. Since ammonia can be decomposed to give hydrogen it is an economical means for transporting hydrogen.

Water Purification. In conjunction with chlorine, ammonia is used to purify municipal and industrial water supplies. The ammonia and chlorine are metered into the water in the desired proportions. The chloramines formed are water purifiers.

DANIEL BERG

Cross-references: *Bases, Amines, Amides, Noxious Gases*

AMPEROMETRIC TITRATIONS

An amperometric titration is a regular titration in which the equivalence point is determined by measuring the $300 \mu A$ current which flows through the system as the result of imposing a constant voltage across two electrodes in the solution. The location of the equivalence point is determined from a graph of current vs. milliliters of titrant. Usually it occurs as the intersection of two straight lines. Therefore, it is not necessary to give any special concern to the area around the equivalence point during the titration. The intersection of the two straight lines is readily accomplished by dependable extrapolation.

The diffusion current measured is the result of an electrode reaction taking place under the driving force of the applied voltage, and is proportional to the concentration of the electroactive species. The electrode reaction may involve the species being titrated, the titrant, the product of the reaction of either, or of an "indicator". Each situation gives a different shaped plot of current vs. volume of titrant. The titrations may be classified according to the shape of curve which they give.

Classification of Titrations. One type of curve is that obtained when the species being titrated is being oxidized or reduced at the electrode (most of the electrode reactions used are reductions). The current will decrease due to the removal of the species by the titrant. When the titration is complete, the current flow becomes essentially zero and remains zero upon the addition of excess titrant. As an example, consider the titration of lead ion with sulfate. At an applied voltage of -0.65 volt vs. S.C.E. (saturated calomel electrode as a reference) the lead ion is reducible at the dropping mercury electrode, and a diffusion-controlled current is obtained, exactly as in polarographic analysis. Now, when the concentration of lead ion is reduced by reaction with the sulfate to form insoluble lead sulfate, the diffusion-controlled current is decreased accordingly, because it is proportional to the lead ion concentration. This continues until no lead ion remains. No species reducible at the applied voltage of -0.65 volt vs. S.C.E. is then present, and the

current approaches zero and remains so upon addition of excess sulfate. By measuring the current at four or five points both before and after the equivalence point, straight lines may be constructed, and their intersection denotes the equivalence point. Current readings are generally corrected for the volume change caused by the titrant before plotting.

A second type of titration curve involves the titration of a nonactive species with an active (oxidizable or reducible at an electrode) titrant. An example is the titration of barium ion with chromate. Here no current is obtained until all the barium has been precipitated by the added chromate. Then the current will increase as the excess chromate is reduced at the indicator electrode at the applied potential. A third classification is that in which both the species being titrated and the titrant provide a diffusion current by reduction at the indicator electrode. A typical example would be the titration of cupric ion with α -nitroso- β naphthol.

Choice of Applied Voltage. The voltage applied across the electrodes must be sufficient to cause the desired oxidation or reduction reaction to take place. It must not be so high that it causes undesired reactions to occur at the electrodes. In general the potential is conveniently found by examining a polarogram of a solution containing the active ion. A voltage corresponding to the flat, diffusion current portion of the curve is the most desirable. Thus, in the first example, it is desired to have lead ion reduced as long as it is present. A polarogram of lead nitrate indicates a diffusion current occurring due to the reduction of lead between -0.05 and -1.0 volt vs. S.C.E. A polarogram of sulfate does not show any reduction wave in this region. Thus any value in this range would be satisfactory, provided the actual titration sample contains no other reducible ions.

Concentration Range. Polarographic measurement is most commonly made with solutions 10^{-2} to 10^{-6} M. Since the currents obtained in amperometric titrations are the same, solutions of ions in this general range will be the most satisfactory. The wide range is possible by using a series of shunts which makes possible the measurement of definite fractions of the total diffusion current.

Relation to Other Methods. As indicated, amperometric titrations are directly related to polarographic measurement. In effect, it is a polarographic measurement of concentration of the active species after increments of the titration. The method is also related to the "dead-stop" end point. In the latter, two indicator electrodes are used instead of one indicator and one reference as in amperometric. A constant potential applied will cause the electrode reactions to occur. If one of the species necessary for one of the electrode reactions is removed by titration, the current drops to zero at the end point as with the amperometric titration. This cessation of current flow is noted on a sensitive galvanometer.

WARREN W. BRANDT

Cross-references: *Titration, Analytical Chemistry, Polarography*

ANALYTICAL CHEMISTRY

Analytical chemistry is probably the oldest field in the broad spectrum of the science of chemistry. Many years were required to dispel the lure of alchemy; more were needed to demonstrate the fallacy of the phlogiston theory. When, however, the brilliant French chemist, Lavoisier (1743-94) demonstrated, about 1785, by actual experimental methods that combustion was a combination of a substance with oxygen, he laid the basic groundwork of modern chemistry and, in a very particular sense, analytical chemistry. Indeed he can with considerable justification be called the "father" of analytical chemistry because of the great emphasis he placed in all experimental work on quantitative measurement. It is in this very necessary characteristic of the true analytical chemist that he differed from Priestley (1733-1804), the discoverer of oxygen. Priestley, a clergyman forced to flee from Birmingham, England, to America because of his unorthodox political and religious views, was more of a philosopher than a scientist.

The first problem to engage the interest of most chemists was to determine as exactly as possible the composition of the earth. Greater emphasis was perhaps placed on chemistry than on physics at this stage in the evolution of the natural sciences - yet the contributions of such scientists as Avogadro, Boyle, and Charles all had a direct bearing and, therefore, great usefulness in analysis. Avogadro's Law, for example, is extremely important in the chemistry of gases, because it serves as a basis for relating weight to volume. Indeed it is not an overstatement to say that during the 18th and most of the 19th century, the chemistry that did exist was largely analytical chemistry. The pinnacle of ambition of most chemists at that time was to be a highly successful analyst. Any study of the chemical literature of this period shows a preponderance of titles related to analytical chemistry.

This so-called "industrial revolution" took place largely in the latter half of the 19th century. Many beginnings (modest at first) were made in the industrial manufacture of numerous items consumed in the household which were traditionally produced in the home or not at all. The raw materials in such manufacturing operations consisted chiefly of chemicals.

The processing and dyeing of textiles, the production of glass, leather, soap—these are merely four examples (many others could be quoted) of operations that moved slowly out of the home and into the factory. Slowly, but surely, this trend built up a demand for modest changes for a limited number of chemicals. Except for the natural dyes and tanning extracts, most of the industrial chemicals produced in this area were inorganic in nature, principally alkalies, mineral acids, etc.

The relatively small chemical manufacturing plants producing such chemicals as alkalies, sulfuric acid, etc., indeed, some of the factories making consumer goods and employing chemicals in the processing, soon found it desirable to employ

what was most frequently referred to as a "works chemist." His duties consisted largely of performing routine tests to determine the quality of the raw materials coming in, so to speak, the back door, and the finished goods going out the front. In nearly every instance the "works chemist" reported to the factory manager. The analyst's prestige within the organization was largely that of a technician, rather than a person considered to be professional.

The "works chemist" or analyst of this era was concerned almost exclusively with two branches of analytical chemistry, namely, qualitative analysis and quantitative analysis. In qualitative analysis, interest is directed to determining the constituent parts of a given product, without any effort to determine the quantitative relationships of these parts. Quantitative analysis, on the other hand, as the term very definitely indicates, is directly concerned not only with determining the constituent parts, but how much of each is present.

The analyst and the "works chemist" of the 18th and 19th centuries depended almost entirely on what are frequently defined today as the classical methods of analysis, namely, gravimetric analysis and volumetric analysis. Gravimetric analysis is based on methods of determining the weights of the respective constituents of a product, whereas volumetric analysis is based on volumes rather than weights, the volumes being determined by a process known as titration—that is the determination of the strength of acid and basic solutions.

The plight of the so called "works chemist" during the industrial revolution was not the sole reason for the decline in the glamor and prestige of the analyst in the early days of the science of chemistry.

Following a logical sequence of events, it is not at all strange that the chemist, having taken natural substances apart in order to determine their constituent elements, would then begin gradually to think about synthesizing in a test tube, at least some of the useful things found in nature. The next logical step, of course, was to begin to think about producing things *not* found in the natural state. Thus we had an evolution of research, principally in organic chemistry, directed toward synthesizing old or new compounds, chiefly the latter.

About halfway between World War I and World War II, the analytical chemist gradually began to experience a renaissance in his status with other members of the profession and with management. Quality became a very important factor in ever-increasing competitive markets. With this welcome change there came a demand for more rapid and more accurate methods of analysis. This demand led to a tremendous amount of research related to the broad field of analysis. New scientific concepts were introduced, many of them based on what might be called physical chemistry.

The so-called classical gravimetric and volumetric methods have by no means been superseded by physical chemistry and physical methods. Instrumental analysis as it is known today supplements rather than supplants the so-called classi-

cal wet methods. Such terms as colorimetry, spectrophotometry, infrared spectrophotometry, Raman effect, fluorimetry, spectrography, x-ray spectrography, x-ray diffraction, radiometric methods, polarography, etc. are in common usage, and a very part of the analytical work now performed is through the use of instrumentation. Indeed, modifications of many of these instruments are now being moved out into actual manufacturing operations in order to provide continuous analyses.

One of the more modern developments in the field of analysis is that of microanalysis, employed where the size of the samples is considerably smaller than is used in the type of analysis sometimes defined as macroanalysis. Today quite a number of analysts are directly concerned with what is frequently defined as trace analysis. The determination of very low concentrations is often of great importance in maintaining high quality of product. A wide variety of new techniques have been developed to meet this need. Another field currently receiving greater attention is the matter of scientific sampling. Certainly no method of analysis, no matter how accurate, will give a proper perspective if the sample employed is not reasonably representative of the whole.

Today the research analyst in the chemical process industries is an honored member of the "team." The use of this term has become rather widespread to describe the modern "team approach" to the discovery, development, and full-scale production of new products. Thus the wheel of fortune for the analyst has made a complete circle.

WALTER J. MURPHY

Analytical Chemistry of Radioactive Elements

Analytical chemistry has been given tremendous emphasis by the advent of atomic energy. Three factors are responsible: (1) the need for determining traces of many elements in high-purity uranium; (2) the need for separation and characterization of the many isotopes resulting from nuclear fission; and (3) the availability of radioactive isotopes which could be utilized as tracers for studying analytical processes.

Uranium was considered a rare metal until the advent of the Manhattan Project. Since that time, it has been intensively studied and there are more data available on the analytical properties of uranium than on any other element. In addition to analysis for uranium itself, the high purity requirements for reactor uranium mean that suitable methods must be found for determination of traces of almost all the known elements in a uranium matrix. The small concentrations of impurities have required that most of the determinations be carried out instrumentally after suitable chemical separations. Therefore, basic research has been carried out on emission and absorption spectra, electrode potentials, diffusion potentials and many other physical properties of most of the known elements.

The advent of atomic energy has brought several new elements into being, especially the trans-

uranic elements. The requirements for analysis of small quantities of these elements have brought improvements in many microchemical techniques, particularly in physical chemical methods. The periodic analogy of the transuranic elements to those previously known could yield only qualitative conclusions, and quantitative measurements were required on many properties, such as redox potentials and solubilities.

Seaborg in 1946 described chemical analyses involving only 0.1 microgram in volumes as small as 10^{-4} ml, and physical measurements were made on quantities of the same order. Although larger amounts of these elements are now available, the high toxicity of several isotopes still limits the amounts handled to the microgram range.

The mixture of fission products, largely the more common elements plus the rare earths, offers a large source of radioisotopes for chemical research. This, in turn, requires the development of methods for separating the individual elements. The techniques are largely those of analytical chemistry, since clean-cut, small-scale separations are required. While the standard precipitations and solvent extractions have proved quite valuable, the ion-exchange column with synthetic resins has been a major tool. The preferential absorption and elution of various elements in different media has given remarkably sharp separations of even individual rare earths.

Radioactive tracers have been a particular boon to the analytical chemist for the development of new methods and the testing of old ones. In many of the older procedures tested with radioactive tracers, it has been found that correct results had been obtained only by compensating errors. Tracer methods have shown the exact contribution of all the factors concerned.

Radioactivity has three other major applications: radiometric analysis, activation analysis, and the isotope dilution technique. In radiometric analysis, the element to be determined is precipitated with a radioactive reagent. The classic example is the precipitation of traces of chloride with Ag^{110} . The minute quantity of radioactive silver chloride may be collected by coprecipitation with ferric hydroxide and counted.

In activation analysis, a sample is subjected to neutron irradiation in a nuclear reactor. Traces of certain elements may then be determined from the radiochemical properties of the isotopes produced. Another widely accepted technique is that of isotope dilution, where a known amount of a radioisotope of the element determined is added to the original sample. When the final precipitate is collected and weighed, the measure of its radioactivity compared to the added activity gives the yield of the chemical process and therefore allows determination of the total amount of the element initially present.

A corollary of the isotope dilution procedure is applied to analyses for traces of radioisotopes. In this case, the minute quantities cannot be handled and may even give deviations from expected chemical behavior. By dilution with a known amount of an inactive isotope of the element sought, these difficulties may be avoided. If the

final quantity of the element is measured, such as by weighing a precipitate, the per cent recovery of the process may be estimated. This factor may be applied to the measured activity of the product to calculate the total radioisotope initially present.

The atomic energy program has also made available many stable isotopes in pure form as an offshoot of its isotope separation studies. The utilization of stable isotopes has been less spectacular than that of the radioisotopes, but is still important. The spectral shifts given as isotopes of different mass are substituted in a compound have aided the analyst in assignment of infrared absorption bands to specific molecular groupings. Fortunately, isotopes of carbon, hydrogen, oxygen, nitrogen and other light elements are available for these studies.

Atomic energy has presented the analytical chemist with new problems and also with new tools. Both of these have promoted the rapid advance of basic research in analytical methods, and have opened many new fields of development, as well as making possible accurate evaluation of older methods.

J. H. HARLEY

Cross-references: *Gravimetric Analysis, Spectroscopy (Optical), Spectrophotometry, Chromatography, Radioactivity, Fission (Nuclear), Chemistry, History*

ANESTHETICS

Anesthetics are agents which, when suitably applied, cause a general or localized loss of feeling or sensation. General anesthetics exert their action on the higher nerve centers and produce involuntary loss of consciousness. When a suitable agent is applied to peripheral nerve endings (topical anesthesia), by infiltration into the nerve fiber (intra-neural anesthesia), around the nerve sheath (para-neural anesthesia), or into the spinal canal (intra-spinal anesthesia) at various levels, a loss of sensation is produced within a restricted or readily predictable large segment of the body. This type of anesthesia is called local, block or regional anesthesia. It does not produce loss of consciousness but effectively prevents the transmission of certain kinds of pain sensations from any region which lies farther from the brain than the site of application of the anesthetic agent and which is served by the anesthetized nerve.

General anesthetics may be classified according to their physical properties as volatile (gases or low boiling liquids) and nonvolatile (high boiling liquids and solids). Several chemical classes are either potentially or practically valuable as general anesthetics. These include the following useful individuals.

Hydrocarbons. Gaseous and volatile members of the aliphatic series, while potentially anesthetic, have such a low degree of activity that effective concentrations produce dangerous anoxia. None has been found useful.

Cyclopropane or trimethylene may be made from propane by chlorination, fractional separation of

1,3-dichloropropane, b.p. 119°C , from other isomers and cyclization with zinc in the presence of iodide to yield the hydrocarbon. It was first used as an anesthetic in 1920. The anesthetic grade is not less than 99% by volume of C_3H_6 . It is soluble in 2.7 parts of water at 15°C and is freely soluble in fatty oils. It is marketed in cylinders of compressed gas which must comply with the standards described in the United States Pharmacopeia. It is highly flammable and forms explosive mixtures with air or oxygen. One distinct physiological advantage is that it exerts its anesthetic action in the presence of substantial proportions of oxygen. Anesthesia is quickly achieved and consciousness rapidly recovered when the administration is stopped.

Ethylene. The chemical was described as early as 1795 but its anesthetic properties were not reported until 1923. The classical synthesis is achieved by the dehydration of ethanol with concentrated sulfuric acid at about 180°C . Phosphoric acid may be used in a similar reaction as well as the dehydration of ethanol over aluminum oxide at 360°C . Large quantities of ethylene result from catalytic cracking of petroleum. Medicinal grade ethylene is marketed as a compressed, liquefied gas in steel cylinders. It must comply with the standards described in the United States Pharmacopeia. At atmospheric pressure it is soluble (1:4 v/v) in water at 0°C and (1:9 v/v) at 25°C ; it is very soluble in alcohol and in ether. It forms explosive mixtures with air or oxygen but can be administered under suitable safeguards with substantial volumes of oxygen. Anesthesia is quickly induced and recovery is rapid.

Ethers. *Ethyl ether* was discovered as early as 1540 but its first recorded use as a surgical anesthetic was in 1842. Anesthetic grade ether contains 96-98% of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, the remainder being a mixture of alcohol and water. It is marketed as a colorless liquid, boiling point 35°C , in tight containers. It should be used promptly after the container is opened before any substantial amount of ether peroxide may form. This toxic and highly explosive oxidation product of ether results when ether is exposed to air and light for any considerable time. The medicinal grade of ether must meet the tests described under that title in the United States Pharmacopeia.

Vinyl Ether resulted from a calculated effort to prepare a general anesthetic having many of the physiological properties of ethylene and ether. It was synthesized and pharmacologically tested in 1930. The product is marketed as a liquid, b.p. $28-31^{\circ}\text{C}$ which comprises about 96% vinyl ether and about 4% anhydrous alcohol. A trace of an antioxidant preservative is permitted.

Other ethers which are analogous to or isomeric with ether have been used experimentally, among these may be mentioned methyl ethyl ether, methyl propyl ether, methyl cyclopropyl ether, ethyl cyclopropyl ether. None of these has achieved wide use.

Halogenated Hydrocarbons containing one or two carbon atoms and one or more atoms of chlorine have potential and practical anesthetic activity. All of this group are characterized as

toxic when administered over a long period or for repeated shorter periods. The first of this group to be used was chloroform.

Chloroform was first prepared in 1832, but its use as a general anesthetic dates from 1847. The marketed product is 99 to 99.5% pure with alcohol as the permitted impurity. Chloroform boils at about 61°C and is nonflammable and nonexplosive. The periods of induction and recovery are short.

Ethyl chloride was prepared in 1845 and achieved its first use as an anesthetic in 1847-1848. Ethyl chloride is a gas at ordinary room temperature and pressure (b.p. 12-13°C). It liquefies under relatively low pressures and is frequently marketed in specially designed glass ampuls with a valve for withdrawal of the liquefied substance. In this way a stream of liquid may be directed on tissue to anesthetize it by lowering the temperature. Ethyl chloride, and its bromine analog, are sometimes used as inhalation type general anesthetics. Induction and recovery are rapid. Ethyl chloride is flammable.

Trichloroethylene was prepared in 1864 but was first used as an analgesic and general anesthetic about 1933 to 1934. It is a colorless liquid (in commerce sometimes colored blue with an approved medicinal dye) boiling at 88°C. It is not flammable. Induction and recovery periods are short.

Halogenated alcohol. Alcohols containing one hydroxyl group and short hydrocarbon chains are potentially anesthetic, but their potency is largely increased by replacement of several of the hydrogen atoms of the hydrocarbon chain with chlorine or bromine. The latter is particularly effective and is exemplified in tribromoethanol.

Tribromoethanol is a low melting (79-82°C) crystalline compound. The substance is somewhat soluble in water but is usually marketed as a solution in tertiary amyl alcohol (amylene hydrate) of approximately 1 g in 1 ml of solution. The solution is suspended in warm water and administered as a retention enema. It is recommended for use as a basal anesthetic and when complete anesthesia is desired, it is usually supplemented with an inhalation type of general anesthetic.

Nitrous oxide was first prepared by J. B. Priestley in 1772. Its anesthetic properties were observed by Humphry Davy about 1799-1800 but it did not achieve use in surgery until after the dramatic failure of a public demonstration by H. Wells in 1845 had called the attention of dentists and surgeons to its possibilities. It is usually prepared by the thermal decomposition of fused ammonium nitrate at about 240°C.

The gas is freed from possible contamination with nitric oxide (NO) by passing it over iron powder and is then compressed and cooled in three stages to a liquid. The liquefied gas is marketed in steel cylinders. It is required to be not less than 95% pure N₂O with the allowable impurity being nitrogen. It must be administered with some oxygen or air to avoid anoxia. It produces rapid anesthesia and the recovery period is equally short. It is not suitable for prolonged anesthesia nor for surgery which requires profound relaxation.

Barbituric acid derivatives. When administered in the usual manner by mouth and in therapeutic

doses, the derivatives of barbituric acid are sedative and hypnotic but not anesthetic. However, when the soluble salts of these compounds are administered intravenously, they produce typical anesthesia. Many of these barbituric acid salts have such a prolonged action that they are not usable for anesthetics, since one of the desirable properties is that the anesthetist should have rapidly adjustable control over the depth and duration of anesthesia. Those barbiturates which act promptly and are destroyed in the body rapidly make useful general anesthetics. Among those which are frequently used for this purpose are some which contain a sulfur atom in the place of C₂-oxygen and others which have a methyl group in place of the N₁-hydrogen.

Local Anesthetics

It has long been known that lowering the temperature of a portion of the body will make the perception of pain originating in the area of lowered temperature less apparent. Likewise, it is known that pressure applied to a nerve fiber or trunk will interfere with the transmission of pain impulses originating peripherally to the site of the pressure. The first principle is still occasionally used to produce local anesthesia. Advantage is taken of the low temperatures produced by the vaporization of such compounds as ethyl chloride, ether and solid carbon dioxide to produce local anesthesia in restricted segments of the body.

The beginning of the modern period of local anesthesia by physiologically active compounds can be traced to the isolation and characterization of the alkaloid cocaine. This alkaloid was isolated from the leaves of *Erythroxylon coca* by Niemann in 1860. Its local anesthetic effect on the tongue was noted by Wohler. Its use in surgery dates from the work of Koller who, in 1884, described the use of cocaine in surgery of the eye, nose and throat. Koller also used cocaine by infiltration techniques. (See *Alkaloids*).

A systematic investigation of the chemical nature of cocaine led to its synthesis by Willstätter in 1902 and to the development of a large number of synthetic compounds which have valuable local anesthetic action, for example, the procaine group (Novocaine). As a result of much work relating to the chemical constitution of cocaine analogs and local anesthetic activity, a number of general relationships were traced. It was found that alkyl esters of aromatic acids such as benzoic and naphthoic acids had potential local anesthetic activity. This is enhanced by the presence of substituent groups in the aromatic ring such as alkyl, amino, hydroxy, alkoxy and alkylthio. Isosteric compounds such as substituted amides and amidines, as well as thiocarboxylic esters and urethanes retain the anesthesiophore.

Many of the simple alkyl esters of aromatic acids were only useful as topical anesthetics, since their water solubility was too low to permit their use in parenteral solutions. It was found that the inclusion of a tertiary or secondary aliphatic or cycloalkylamine in their structure made it possible to prepare water-soluble salts with acids which

could be administered by parenteral pathways. This was also possible in the case of amides, thio-carboxylic esters and urethanes. Amidines which were of moderately high molecular weight are sufficiently basic to form salts which can be dissolved and used. A large number of individual compounds have been synthesized and a considerable number have been marketed.

Some of these compounds, like cocaine, are effective when applied topically or parenterally. A number are poorly active topically but adequately effective when injected. Many experimental compounds are rejected because of their locally irritant effects or systemic toxicity or both. Other compounds which, structurally, are potentially local anesthetics have found their greatest clinical use for other effects such as antispasmodics.

The local anesthetic effect of quinine salts and Eucupin (isoamylhydrocupreine) should be mentioned. Both quinine hydrochloride, rendered more soluble with urea, and Eucupin have been used where local anesthesia of long duration was desired.

A number of simpler compounds such as Chlorbutanol (1,1,1-trichloro 2 methylpropanol 2), benzyl alcohol and salicyl alcohol have mild local anesthetic effects when topically applied to mucous membrane

G. L. WEBSTER

Cross-references: *Ethers, Oxides, Alkaloids*

ANHYDRIDES

The term "anhydride" means "without water." Thus an acid anhydride is a compound that lacks the water necessary to make it become an acid.

Inorganic Anhydrides

Oxides, usually those of nonmetals, that react with water to form acids are called acid anhydrides or acid oxides. Sulfur dioxide (SO_2), carbon dioxide (CO_2), phosphorus pentoxide (P_2O_5), and sulfur trioxide (SO_3) are examples of such oxides. $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ and $\text{P}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HPO}_3$ are typical reactions of acid anhydrides with water to form acids.

Oxides, usually those of metals, that react with water to form bases are called basic anhydrides or basic oxides. Calcium oxide (CaO), sodium monoxide (Na_2O), and chromous oxide (CrO) are examples of such oxides. The reaction $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$ (the slaking of lime) is one of the most definite examples of the reaction of a basic anhydride with water to form a base. It is obvious that a rather limited definition of the terms acid and base is assumed in this description.

For some metals that have several states of oxidation, chromium and manganese being the most common examples, the oxides in which the metal has the lower oxidation values are basic anhydrides; the oxides in which the metal has intermediate value are amphoteric; and the oxides in which the metal has higher oxidation values are acid anhydrides. The explosive compound, manganese heptoxide (Mn_2O_7), and manganese trioxide (MnO_3), which has doubtful existence,

are acid anhydrides that form the permanganate ion (MnO_4^-) and the manganate ion (MnO_3^-), respectively, when they react with water. Manganese dioxide (MnO_2) is somewhat amphoteric. Manganese sesquioxide (Mn_2O_3) and manganous oxide (MnO) are basic anhydrides. In these five oxides, the oxidation number of the manganese is respectively 7, 6, 4, 3, and 2. A similar pattern exists for the oxides of chromium. Chromous oxide (CrO) is a basic anhydride, and chromium trioxide (CrO_3) is an acid anhydride.

Organic Anhydrides

Organic anhydrides seem to have been made by combining the residue of two carboxyl ($-\text{COOH}$) radicals by means of an oxygen atom when water is eliminated between the two carboxyl radicals. Thus two molecules of acetic acid form acetic anhydride. A molecule of water is eliminated from two molecules of acetic acid. The use of anhydrous calcium sulfate (CaSO_4) aids the dehydration. Anhydrides generally hydrolyze slowly in cold water, more rapidly in warm water, and readily in alkaline solution.

Acetic anhydride, boiling point 139.6°C , is by far the most important of the organic acid anhydrides. It is an aliphatic anhydride that is characterized by a sharp penetrating odor. Production each year in the United States is in the order of one half million tons. Synthetic methods are used.

Acetic anhydride is used to introduce the acetate radical into organic compounds, and is called an acetylating agent. About three fourths of the acetic anhydride made is used to make cellulose acetate. Cellulose acetate in turn is used to make fibers ("Celanese," "Acete," etc.), plastics, photographic films, and transparent wrapping sheets. Acetic anhydride heated with salicylic acid ($\text{C}_6\text{H}_4-\text{OH}-\text{COOH}$) forms acetylsalicylic acid (aspirin). In general, alcohols react with acetic anhydride to form an ester and acetic acid. For example: $\text{C}_2\text{H}_5\text{OH} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{CH}_3\text{COOH}$.

Phthalic anhydride, a colorless solid, melting point 130.8°C , is the leading aromatic anhydride. Its annual production in the United States exceeds 100,000 tons, and it is about one fifth of the weight of acetic anhydride produced annually. It is the anhydride of *o*-benzenedicarboxylic acid. Commercial manufacture is carried out by careful partial oxidation of naphthalene (C_{10}H_8) in the presence of vanadium pentoxide (V_2O_5) as a catalyst. An anhydride of a polybasic acid, it polymerizes with polyhydroxy alcohols and forms resins of the alkyl type.

Glycerol [$\text{C}_3\text{H}_8(\text{OH})_3$] and phthalic anhydride form the well-known thermosetting "Glyptal" resins known for their resistance to electricity and their use in paints and other surface coatings. Phthalic anhydride is also used to make phthalate plasticizers, anthraquinone, phthalimide, anthranilic acid, phenolphthalein, xanthene dyes, and benzoic acid.

In a manner similar to the oxidation of naphthalene to yield phthalic anhydride, the controlled catalytic partial oxidation of benzene yields maleic anhydride, another cyclic anhydride.

Maleic acid ($\text{COOH}-\text{CH}=\text{CH}-\text{COOH}$) is changed to maleic anhydride by heating. In this reaction the ring is closed by means of an oxygen atom. Such ring formation takes place when the two carboxyl ($-\text{COOH}$) groups are separated by two or three carbon atoms. Malonic acid ($\text{COOH}-\text{CH}_2-\text{COOH}$) forms no anhydride of this type, but merely heating succinic acid ($\text{COOH}-\text{CH}_2-\text{CH}_2-\text{COOH}$) changes it into succinic anhydride, thus forming a ring compound. Maleic anhydride is used to make alkyl resins.

ELBERT C. WEAVER

Cross-references: *Acids, Bases, Oxides*

ANNEALING

Annealing is the process by which uncontrolled strains are removed from glass or metal products. In the manufacture of glass, articles are shaped from the viscous liquid by pressing, rolling, drawing, blowing or casting. During this forming process the material is cooled rapidly and irregularly so that large temperature gradients are present as the viscosity increases and the liquid becomes a rigid solid. In the liquid, any strains caused by the forming operation disappear very quickly, so that the article is essentially free from strain when it first becomes solid. In this respect, glass products differ from many metal articles in which strains due to such forming operations as stamping, drawing or spinning must be removed by annealing. However, when the temperature gradients existing in the newly formed solid glass disappear through its cooling to the ambient factory temperature, strains are created by the unequal contraction of different parts. In general those parts of the glass article which cooled slowest contract most after solidification, and are thrown into tension, while those parts which cooled fastest contract less and are compressed by the rest of the glass.

Glass never breaks because of compressive stress, but the parts which are under tension are quite unstable. Even if the piece survives cooling, it is likely to fly into bits at the least touch upon a sensitive tension surface. Fortunately, surfaces, particularly outside surfaces, tend to cool first and consequently are often in compression, so that unannealed glass articles may appear quite strong until a sensitive tension spot is touched. Indeed, as we shall see later, controlled disannealing of glass may be employed to increase its strength and serviceability.

In sheet glass, which must be cut into panes for glazing purposes, strains even of a compressive nature are quite unacceptable, since cutting is really a cracking operation and strains either prevent the crack from running or cause it to stray from the desired course. Also strains in flat glass result in warping which itself prevents satisfactory cutting on a flat table.

Strains are present not only in newly formed glass articles, but also in articles which are reheated in spots for any reason, if the reheating is sufficient to soften the glass, even though the articles may have been previously well annealed.

Such operations as fire polishing, reshaping, and sealing require subsequent annealing.

Sometimes the term "tempering" is used to mean annealing, but it actually means the process of controlled disannealing. Annealing may be either a batch or a continuous operation. In the earliest times, glass articles were placed in a chamber above the melting furnace to equalize the temperature and cool them slowly. Later, batch ovens were built for the purpose, some of which are still used, particularly for large or thick pieces, which require very slow cooling, and for optical glass, which also requires extended heat treatment.

However, most glass is now annealed in a continuous oven called a "lehr" which has the form of a long narrow tunnel. Pressed and blown articles are carried through the lehr on some sort of conveyor or belt, while flat glass passes through on rollers in a continuous sheet as it is produced by drawing or rolling. Where the glass is drawn vertically, as in the Fourcault process, the lehr is necessarily vertical and is therefore of limited length. In any case the lehr is provided with burners, dampers, muffles and temperature control equipment so that glass passing through it may be subjected to a predetermined and carefully controlled heat treatment to relieve strains.

In order to observe and measure the state of strain in glass to find whether it is well annealed or dangerously unstable, advantage is taken of the fact that strain causes a proportional birefringence in glass. The retardation measured in a suitable polariscope gives a figure for the average difference in the principal stresses perpendicular to the light path when the constant of proportionality, which is known as the stress optical coefficient, has been determined.

Since the strain in glass is due to the temperature gradient existing as it solidifies, strain may be practically eliminated by bringing the glass to a uniform temperature high enough to cause it to behave as a liquid, and then cooling it with as little temperature gradient as possible. With modern, high-speed production of glass it is obviously desirable to minimize the time required by the annealing step, and this introduces problems. At first sight it would seem desirable to heat the glass to as high a temperature as possible without deforming it, in order to relieve the strains quickly. However, cooling is possible only by establishing a temperature gradient which causes an immediate temporary strain. In rigid glass such temporary strain would disappear when cooling ended and the temperature become uniform. In fluid glass the temporary strain is relieved by flow, and a corresponding and opposite strain appears when the temperature becomes uniform at the end of the cooling. Hence to minimize the strain reintroduced by the cooling step, it is desirable that the viscosity be high, that is that the temperature be low, and that the rate of cooling be slow. Under these circumstances it is obvious that there will be an optimum temperature for the relief of strain in the annealing process.

The strain reintroduced in cooling is proportional to the expansion of the glass and the square

of the thickness and inversely proportional to the thermal diffusivity and the elastic constant. Using these relationships the optimum temperature for relieving stress and the optimum cooling rate may be found.

In annealing optical glass, not only must the residual strain be very low, but also all parts must be given a sufficient heat treatment to render the refractive index uniform throughout. This may be done by cooling it at a constant rate from a relatively high temperature at which the equilibrium index is reached very quickly by all parts. The cooling rate must be slow enough to avoid introducing too much strain and must be constant through the range in which the index varies with time, so that all parts of the glass cool at the same rate, the surfaces first and the center last. When using this method the index may be adjusted by changing the rate of cooling.

Although annealing is usually thought of as a means of preventing glass from breaking, a controlled disannealing is very effective in increasing its strength. If the cooling is arranged so that the total surface of a piece of glass is in compression, failure can occur only when the tensile stress due to a blow or other service condition overcomes this compression. Of course, the interior of the piece where the glass is in tension must be free from crystals or other defects which might originate a fracture. This method of strengthening glass is known as *tempering* or *chilling*.

C. H. GREENE

Cross-references: *Glass*

ANTIBIOTICS

Definition. Antibiotics are chemical substances produced by microorganisms; in dilute solution, they have the capacity to inhibit the growth of and even to destroy other microorganisms. Numerous attempts have been made, unjustifiably, to broaden the definition of antibiotics so as to include antimicrobial substances of plant and animal origin, on the one hand, and synthetic material, on the other.

Antibiotics are produced by various groups of microorganisms, particularly bacteria, fungi, and actinomycetes. The ability to produce antibiotics is characteristic not of the genus, nor even of the species, but of strains of particular organisms. Among the actinomycetes, as many as 50 per cent of all cultures isolated from the soil are able to produce antibiotics when grown on suitable media and tested under favorable conditions. Identical antibiotics are sometimes produced by different species. Some species are able to produce more than one antibiotic.

Specific media and special conditions of cultivation are required for the production of antibiotics. Most of the media favorable for antibiotic formation contain complex organic substances.

Antibiotics vary greatly in chemical nature, physical properties, selective activity upon bacteria and other microorganisms, toxicity to animals, and *in vivo* activity. The selective action of antibiotics is spoken of as the *antibiotic spectrum*.

Some microbes are sensitive to a given antibiotic, and others are resistant. The degree of sensitivity is qualitative and quantitative in nature. Some are active largely upon bacteria and some upon fungi, others are active on both bacteria and fungi. Still others are also active upon the larger viruses. Some are active upon protozoa. Some antibiotics have found extensive application as chemotherapeutic agents in the treatment of numerous infectious diseases in man, animals, and plants.

Historical background. The ability of certain microorganisms, especially bacteria and fungi, to inhibit the growth of other microbes has been known since the latter part of the last century. The activity of green molds, belonging to the genus *Penicillium*, upon various bacteria has been known since 1874. This is also true of the effect of various non spore-forming and spore-forming bacteria upon other bacteria, including disease-producing organisms. Attempts were made to utilize the products of such microorganisms in the treatment of various infectious diseases, including tuberculosis. A degree of success was attained with certain bacterial preparations, such as pyocyanase, and with certain mold preparations. The results were not sufficiently clear, however, to justify broad generalizations.

In 1939, R. Dubos isolated from a spore-forming soil bacillus certain polypeptides, described as gramicidin and tyrocidine (tyrothricin), which were found to possess remarkable antimicrobial properties and were active both *in vitro* and *in vivo*. These could be used in the treatment of certain infectious diseases. This discovery was soon followed (1940) by Florey and Chain's study of the formation of penicillin (originally observed and named by Fleming in 1928) by a culture of *Penicillium notatum*, and Waksman and Woodruff's isolation, the same year, of actinomycin, the first true antibiotic produced by a culture of an actinomyces.

The three major groups of antibiotic-producing organisms were thus recognized. These substances have found extensive application in the treatment of numerous infectious diseases. Their discovery has led to tremendous developments in the field of chemotherapy and produced a revolution in medical practice. They have also found extensive application in veterinary medicine, in the treatment of certain plant diseases, in animal feeding, and in the preservation of various biological materials.

These antimicrobial substances were first designated as lysins, toxins, antibacterial agents, bacteriostatic and bactericidal substances, lethal or staling principles. The word *antibiotic* was first used in this sense by Waksman in 1942.

Production. The most important groups of antibiotic-producing organisms are the bacteria, lower fungi or molds, and actinomycetes. Members of the genus *Bacillus*, among the spore-forming bacteria, and of the genus *Pseudomonas*, among the non-spore formers, are extensive producers of antibiotics. Among the fungi, the genera *Penicillium* and *Aspergillus* are particularly important; the ability to produce penicillin belongs to a few

strains of certain species of these genera. Other strains and even other groups of molds may be able to produce penicillin-like substances, but the yields are so low that they cannot be considered on a par with the important commercial producers. Formation of streptomycin and of other important antibiotics is characteristic of certain species of *Streptomyces*.

Some microbes are capable of producing more than one antibiotic. *Pseudomonas aeruginosa* produces pyocyanase, pyocyanin, pyolipic acid, and certain pyo-compounds. *Streptomyces griseus* produces not only the antibacterial substances streptomycin, mannosestreptomycin, and grisein, but also the antifungal substances actidione and candicidin, the antiprotozoan agent streptocin, and certain other antibiotics. Another actinomycete, *Streptomyces fradiae*, produces several forms of neomycin, and fradicein. *Streptomyces rimosus* produces oxytetracycline and rimocidin.

Some antibiotics have been modified chemically to yield substances with somewhat different, perhaps more desirable, properties, as in the formation of dihydrostreptomycin from streptomycin. Only a few antibiotics, notably penicillin and chloramphenicol, have been synthesized, chemically.

Most of the antibiotics produced by bacteria are polypeptides. The most important of these are tyrothricin, bacitracin, subtilin, and polymyxin. The fungi have yielded only one important group of antibiotics, the penicillins. The other antibiotics of fungi include clavacin (claviformin, patulin), citrinin, viridin, fumagillin, and gladiolic acid. Actinomycetes are now known to produce nearly 200 compounds or preparations that possess remarkable antimicrobial properties. These include the actinomycins, the streptomycins, chloramphenicol, the neomycins, the tetracyclines, erythromycin, carbomycin, viomycin, trichomycin, nystatin, candicidin, and numerous others.

Isolation. Once an organism has been selected for the production of a particular antibiotic, the next step comprises the development of suitable media and of conditions favorable for growth and the production of the antibiotic. The antibiotic-producing culture is transferred through a series of stages from the test tube to small fermenters and finally to large tanks. The final stage of growth usually lasts 2 to 4 days, when the concentration of the antibiotic reaches a maximum. The assay of the concentration of the antibiotic is carried out by a suitable microbiological or chemical method against a known standard. When the antibiotic has finally been isolated and purified, a registered standard is established by the Antibiotics Control Division of the Food and Drug Administration in Washington.

Chemical Nature. Antibiotics vary greatly in chemical composition. On the basis of their elementary chemical composition they have been grouped as follows:

I. Compounds containing C, H, and O, such as clavacin ($C_7H_8O_4$).

II. Compounds containing C, H, O, and N. These include such compounds as pyocyanin

($C_{11}H_{10}O_2N_2$), streptomycin ($C_{21}H_{39}O_{12}N_7$), and actinomycin ($C_{11}H_{16}O_{11}N_8$).

III. Compounds containing C, H, O, N, and S. Here belong the penicillins ($R-C_9H_{11}N_2O_4S$).

IV. Compounds containing chlorine, including chloramphenicol ($C_{11}H_{12}N_2O_6Cl_2$) and chlortetracycline ($C_{22}H_{34}N_2O_6Cl$).

Antimicrobial Activities. Antibiotics vary greatly in their ability to act upon different groups of microorganisms. Some are active only upon bacteria and actinomycetes but not on fungi. Others are active only upon fungi but not upon bacteria and actinomycetes. Some have a very wide spectrum, being active against bacteria as well as upon fungi, or upon bacteria, rickettsiae, and larger viruses. Others, like viomycin, have a very narrow spectrum, being active only upon mycobacteria.

The antimicrobial spectrum is of great importance in characterizing an antibiotic and in deciding upon its importance as a chemotherapeutic agent. Penicillin is active upon cocci and various gram-positive bacteria and spirochaetes, but it has little activity against the gram-negative rod-shaped bacteria and the acid-fast bacteria. Streptomycin is active against gram-negative and the gram-positive bacteria, including those causing tuberculosis, but not against fungi and viruses. The tetracyclines are highly active against many bacteria, rickettsiae, and the larger viruses. Some antibiotics, like candicidin, nystatin, trichomycin, ascocin, and chromin are active primarily against fungi. Certain microorganisms are also capable of producing substances that inhibit the growth of or destroy viruses, including phages and tumor cells. Among the antibiotics active upon neoplasms, one may include the actinomycins, azaserine, sarkomycin, and calzinophilin.

Mode of Action and Development of Resistance. Antibiotics are largely bacteriostatic (growth-inhibiting) agents, although some are markedly bactericidal (cell destroying). Some antibiotics are highly toxic to animals; others, notably penicillin, are relatively nontoxic. Some, like tyrothricin, are hemolytic, others are not. Some are readily absorbed from the digestive tract, and others are not.

Upon continued contact with a given antibiotic, originally sensitive bacteria become resistant to it. As a result of this, freshly isolated cultures of micrococci or staphylococci which originally were highly sensitive to penicillin may have gradually become resistant, largely because of the constant use of this antibiotic. *Mycobacterium tuberculosis*, the causative agent of various forms of tuberculosis, originally sensitive to streptomycin may develop resistance to it when in contact with it or when isolated from patients treated with it. A culture of an organism that has become resistant to one antibiotic may remain sensitive, however, to other antibiotics.

There is a certain degree of cross resistance among certain groups of antibiotics, such as the tetracyclines. As a result, an organism made resistant to chlortetracycline automatically becomes resistant to oxytetracycline. To overcome the development of resistance, two antibiotics may be

combined. A combination of streptomycin and penicillin is used in the treatment of certain mixed infections. Sometimes an antibiotic is combined with a chemical compound, as the sulfa drugs or isoniazid.

Antibiotics as Chemotherapeutic Agents. During the last 15 years several hundred antibiotics have been isolated. Only about twenty of these have found a place as chemotherapeutic agents. These include penicillin, streptomycin and its chemical derivative dihydrostreptomycin, chloramphenicol, chlortetracycline, neomycin, oxytetracycline, viomycin, tetracycline, erythromycin, carbomycin, bacitracin, tyrothricin, polymyxin, nystatin, trichomyacin, and a few others.

Some of these antibiotics, like penicillin, are used against a large number of infections caused by various cocci, gram-positive bacteria, and spirochetes. Others, like streptomycin and the tetracyclines, are used against diseases caused by gram-negative bacteria, such as infections of the urinary tract, or those caused by gram-positive bacteria that have become resistant to penicillin. Some antibiotics are specific for certain diseases, such as streptomycin for tuberculosis, chloramphenicol for typhoid fever, the tetracyclines for typhus fever and other rickettsial diseases. Some antibiotics are given by injection, others by mouth. Some are used for skin, eye, and ear infections, others for generalized infections.

As a result of the introduction of antibiotics, most of the diseases of childhood have virtually disappeared, many of the infections of adults have lost their dangerous implications, and the average life expectancy of man has been increased by 10 to 20 years. Tuberculosis, which only 15 or 20 years ago was the number one killer of the human race is gradually coming under control. The effectiveness of antibiotics in the treatment of true virus diseases and tumors is still uncertain.

Many antibiotics cause allergic and other reactions. In some patients streptomycin may cause dizziness, loss of balance, or loss of hearing. This can usually be avoided by reducing the dosage or by combining streptomycin with dihydrostreptomycin or with certain chemical agents. The tetracyclines, taken by mouth, may cause nausea, development of fungus infections, and certain other undesirable reactions. These reactions can be largely overcome by switching to another antibiotic.

Antibiotics have found many other applications, principally in the treatment of diseases of animals, such as mastitis in cattle and various infections in poultry; certain bacterial diseases of plants, such as apple and pear blight; feeding of nonherbivorous animals, and the preservation of biological materials, such as virus vaccines and semen of animals.

Manufacture. The manufacture of antibiotics has increased from a few dollars a year in 1940 to a tremendous industry amounting to nearly a billion dollars a year in the U. S. alone. Penicillin is the leading antibiotic, streptomycin and dihydrostreptomycin take second place, and the tetracyclines and chloramphenicol third place. Neomycin, bacitracin, polymyxin, erythromycin,

fumigallin, and tyrothricin are produced on a much smaller scale. The production abroad is probably as great as, if not greater than, in this country. It is said that nearly 50 per cent of all prescriptions sold over the counter in drug stores throughout the country are now made up of antibiotics.

SELMAN A. WAKSMAN

Production by Fermentation

In the production of antibiotics by fermentation the primary purpose is to obtain the maximum yield of the antibiotic, based on the material consumed, and in high concentration. The growth of the organism is a secondary matter unless growth is directly connected with the yield of the antibiotic.

Penicillin. The first antibiotic to be produced commercially was penicillin. The organism, *Penicillium notatum* Westling, was grown on the surface of the nutrient medium, and relatively small yields of penicillin were obtained. With the development of submerged fermentation, the use of more satisfactory media for growth of the organism, the development of more productive strains by carefully selecting the organism, such as the selection of *P. chrysogenum*, and improvement of strains by mutations induced by x ray, ultraviolet light, and nitrogen mustard, yields of penicillin have been increased to 2,000 μ per milliliter.

Penicillin may be regarded as a metabolic product, but a minor one. A number of other organisms also produce it. Penicillin as produced by mold cultures does not represent a single compound but rather a group of closely related compounds which have a common β lactam-thiazolidine structure with different side chains. Penicillin G was the first penicillin to be isolated, and it possesses highly desirable characteristics for recovery, purification, and therapeutic use.

Factors contributing to high penicillin yields are adequate, effective aeration, the presence, at nontoxic levels, of precursor realized by intermittent feeding, preferably phenylacetic acid or some derivative of it, and the use of organic acids. Mold growth is directly correlated with penicillin yields. The pH of the medium may have a range of 4.5-6.0 during growth in the presence of readily available nutrients, such as ammonium ions, organic nitrogen in corn steep liquor, phosphates, and glucose. When the growth of the organism is completed, the pH is raised to approximately 7.0, and a slowly assimilable carbohydrate, such as lactose is made available. Growth is minimal, and penicillin formation then proceeds. Fermentations are carried out in fermenters of 20,000-30,000 gallons capacity. Sterile air is necessary. Calcium carbonate may be added to control pH during growth.

One of the great advances in the growth of the organism resulted from the use of corn steep liquor which supplies satisfactory nutrients for the organism.

The carbon dioxide of the effluent air from the fermenter may be utilized as a guide to the amount of growth and metabolic activity of the fungus,

and as a function of the amount of aeration supplied. The ammonia nitrogen decreases during penicillin formation and rises slightly toward the end, lactic acid is consumed, the pH rises, the lactose disappears, and autolytic changes in the mycelium may take place. Synthesis of penicillin appears to be associated with an unbalance of the metabolism.

Streptomycin. Another group of organisms, the Actinomycetes, contains several important species that produce streptomycin, chloramphenicol, Aureomycin, erythromycin, and Terramycin. Several other antibiotics produced by Actinomycetes have achieved importance. In his early work Waksman used glucose, peptone, beef extract, and sodium chloride to grow *Streptomyces griseus*. For large scale production in fermenters soybean meal has replaced beef extract and peptone as source of nitrogen. Dextrose, distillers' solubles or corn steep liquor, and calcium carbonate are also employed, the latter to control pH; lard oil and other fats may replace glucose and starch. Yields are said to increase if the histamine like substances from corn steep liquor are removed. The use of actinophage resistant strains to improve yields has been reported. Dextrose may be replaced by animal and vegetable oils. Aeration of submerged cultures is practiced in growing the organism. The fermentation falls into two stages. During the first stage mycelium is formed; lactic acid increases, then decreases, and Streptomycin formation develops. The pH rises, accompanied by lysis.

Chloromycetin. The constituents of the nutrient medium for growing *Streptomyces venezuelae* n. sp., the organism that produces chloramphenicol, in the laboratory are glycerol, meat extract, tryptones, soybean protein, distillers' solubles or molasses and salt. It has been reported that a medium containing starch, peptone, and inorganic salts gives good results. Phenylalanine, tyrosine and methionine are stated to enhance yields of chloramphenicol. Aeration and submerged growth are practiced. Production of mycelium and Chloromycetin run parallel. The chemical composition and structure of chloramphenicol have been established. It has been produced commercially chiefly by chemical synthesis.

Aureomycin. Aureomycin is produced by *Streptomyces aureofaciens*. Commercially, it is stated, corn steep liquor, sucrose, $(\text{NH}_4)_2\text{HPO}_4$, KH_2PO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, traces of Mn, Cu, Zn, and CaCO_3 may be employed. The pH of the medium initially varies from 6.0-6.4, and may fall to 4.5-4.8. Media containing peanut oil meal or peanut meal with a low fat content, 0.2-0.3 per cent $(\text{NH}_4)_2\text{SO}_4$, and 3 per cent glucose gave yields of 2300 μ /ml. An addition of 0.1% molasses gave further increase. Aeration and submerged growth are employed. The chemical structure of Aureomycin was reported in 1952.

Terramycin. Terramycin is a product of *Streptomyces rimosus*. Information indicates that soybean meal, corn starch, N-Z Amine B, NaNO_3 , and CaCO_3 may be used as a nutrient medium. Aeration and submerged growth are practiced commercially. The pH of the nutrient medium is adjusted to 7.0 before sterilization and may rise

to 8.0. The chemical structure of Terramycin was published in 1952. It was found to be oxytetracycline.

Erythromycin. Erythromycin is a broad-spectrum antibiotic produced by *Streptomyces erythreus*. It is now produced commercially by fermentation. Its structure has not been elucidated. The crystalline compound is stated to have the empirical composition: $\text{C}_{39}\text{H}_{71}\text{NO}_{12}$. The U. S. Patent, 2,653,899, to Eli Lilly & Company describes the production of erythromycin by fermentation. It can be produced by submerged fermentation in a soybean-corn steep glucose medium. The range of pH is 6.4 to 7.2.

Bacitracin. Bacitracin is produced by a bacillus, *B. licheniformis*. The antibiotic is a polypeptide which accumulates in the liquor in which the cells grow. Aeration is employed when using submerged growth. Surface growth can be used when aeration cannot be practiced. Soybean or peanut meal, dextrose, sucrose and starch may be employed as growth media.

Other antibiotics less widely used are Actidione (cycloheximide), circulin, fumagillin, magnamycin (carbomycin), neomycin, polymixin, tyrothricin, and viomycin.

CHARLES N. FREY

ANTIBODIES AND ANTIGENS

The name *antibody* implies that a body is acting against an introduced substance. The introduced substance which generates the antibodies is called the *antigen*. Animals have the ability to resist certain infections when they have been previously exposed to them. The existence of antibodies in the blood was originally postulated to account for this immunity to repeated bacterial infection.

Antibodies are serum proteins of the globulin fraction and generally with the physicochemical properties of the γ -globulin of the species producing it. In the rabbit and man they have molecular weights of about 160,000. Antigens are always molecules of at least 10,000 molecular weight and almost always proteins. However, some lipides and polysaccharides can induce antibody formation under certain circumstances. Antigens lose their antigenicity when they are administered orally and, consequently, they are injected parenterally in order to produce antibodies. In general, the antibodies produced in response to one antigen are specific in that they are capable of reacting only with the homologous antigen or those with great similarities in molecular structure.

By means of this action of the antibody the animal has the capacity to destroy the virus or the bacteria. The principle of antibody response it is hoped, but without success thus far, will be of benefit in the fight against cancer, just as it can be used to destroy the viruses causing polio. The work of Karl Landsteiner is responsible for our understanding of human blood groups which arise from antigenic considerations. This work demonstrated that the specificity of the antibody-antigen reaction is not due to the antigen molecule as a whole, but only to certain chemical groupings. He

discovered that an animal can manufacture antibodies with the power to combine with well-defined chemical groups. He used the technique of coupling diazotized amines to proteins. One which has been used extensively is *p*-aminophenylarsonic acid, whose diazonium salt has been coupled to foreign serum proteins. Landsteiner found that antibodies manufactured against the *D*-tartaric acid grouping do not react with the *L* form. He also found that proteins coupled to *o*-, *m*-, and *p*-aminophenylsulfonic acid produce different antibodies.

Not all types of groups are capable of inducing antibodies against them. Only polar groups, such as $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{AOH}_2$, and quaternary ammonium groups appear to have this capacity. It is probable that antigen specificity arises from a particular configuration of a single chemical group like the above, or a given arrangement of several of them. There may be many such groups incorporated into the natural protein, making up the so-called antigen valence. It is believed that the antibody molecule has one or more regions with structures complementary to these, and consequently, that the forces responsible for combination of antibody with antigen are electrostatic, van der Waals, and hydrogen bond type. The antibody may be formed by a unique folding of the peptide chains so as to make available certain chemical groupings on the resultant molecule.

Although the site of formation of the normal serum globulins is not known, it is believed that they arise in the reticuloendothelial cells of the liver, bone marrow, and spleen. There have been many theories proposed for the mechanism of formation of the antibody, and it is generally accepted that the antibody is a new globulin, synthesized under the influence of a nearby antigen. Pauling has gone a few steps further and has described a theory in which the antibody is formed from the precursor of the globulin molecule—that is to say, the amino acid sequences are all the same, but the antibody differs in the way in which the molecule is folded. As the folding occurs, two parts of the chain are in direct contact with the antigen molecule and fold in stable configurations which would be different if the antigen were not present. Consequently, Pauling postulates bivalency for antibody molecules. According to this concept it may be possible to manufacture antibody molecules *in vitro*. This has not yet been accomplished.

Immunochemists have studied the formation of the antibody and its reactions with the homologous antigen to gain understanding of the immunity mechanism. As is not uncommon, their efforts have probably contributed as much to the knowledge of the physical and chemical nature of proteins as to their original thesis. Chemists are presently studying the reactions of antibodies with antigens, using for this purpose the earliest tool, the precipitin reaction, as well as light scattering, ultracentrifuge, and electrophoresis techniques.

The precipitin reaction can be studied by observing the results of adding a constant amount of antibody or antiserum to each of a series of test

tubes containing increasing amounts of antigen (usually increasing by a factor of 2). The reverse can be accomplished by adding constant amounts of antigen to varying amounts of antibody. If the proper relative amounts are chosen, the former test will show maximum precipitation in the center tube and decreasing to either side. Real inhibition to precipitation has occurred on the antigen excess side of maximum precipitation, while the decrease on the other side may be the result of inhibition due to antibody excess or merely lack of sufficient antigen to cause precipitation. To find out which is the case, one performs the latter test, and if real inhibition exists, precipitation will rise through a maximum and then decrease as the amount of antibody increases. Equine antibodies show a pronounced antibody excess inhibition, whereas rabbit antibodies do not. All systems show antigen excess inhibition. The precipitates can be evaluated to determine the amount of antibody and antigen present. The precipitation and inhibition phenomena have been the subject of a great deal of work in recent years in the attempt to reveal the mechanism of the precipitin reaction. It is hoped that this information will eventually lead to an understanding of antibody manufacture and its duplicating mechanism which may not be unlike those which produce replicas of complex biological molecules, for instance viruses and genes.

Ultracentrifugation and electrophoresis have been used to study the antibody-antigen system in the antigen excess inhibition region. In the schlieren diagrams which have been obtained, one finds that the number of peaks approaches 2 as the antigen excess of the system increases. These two peaks represent the free antigen component and the complex component containing the aggregate composed of one antibody and *g* antigens. Analysis of these peaks leads to values of *g* greater than 1, which proves that for the system studied the predominant antibody has a valence greater than 1. Until these new tools had been brought to focus on this problem there had been considerable controversy over this point. By these methods of analysis the equine antibody (manufactured against human serum albumin) has the predominant valence of 2. Unfortunately, workers in different laboratories have not yet agreed on the valence of the rabbit antibody (manufactured against bovine serum albumin). Some contend the valence is 2 and others contend that it is greater than 2. More precise determinations of the schlieren diagrams are required, but the evidence seems to be in favor of 2 at present.

The effects of ionic strength and pH are giving indications of great usefulness in determining the nature of the forces involved in the antibody-antigen bond, again with the use of ultracentrifugation and electrophoresis. Light scattering appears able to contribute usefully to the kinetics of the system. The preliminary results now at hand indicate that significant information regarding the nature of the antibody will be forthcoming in the next few years.

RICHARD J. GOLDBERG

Cross-references: *Bacteriology, Immunology, Blood, Lipides, Proteins*

ANTIFREEZE AGENTS

Water is an excellent heat transfer medium since it has a high specific heat and a very low cost. However, it has two disadvantages: namely, its high freezing point and its corrosive action on ferrous metals in presence of air.

The 32°F freezing point of water is lowered by the addition of various compounds. The extent of lowering is generally indicated by Raoult's law. Thus, it is possible to employ an aqueous solution as a coolant well below the freezing point of water. These aqueous antifreeze solutions serve as means of transmitting heat from one part of a system to another without change of state over the operating temperature of the system. The properties of the binary system, antifreeze agent water, determine the operating temperature range for a particular solution. The critical properties of the system are freezing point, boiling point, heat capacity, viscosity and specific gravity. The most important of these are the freezing point and boiling point composition curves, since these establish the operating temperature range for the system. Other properties (for example, viscosity) may further limit the useful range of a specific solution.

The earliest antifreeze agents consisted of aqueous brine solutions such as sodium chloride, magnesium chloride and calcium chloride. The eutectic temperature for aqueous sodium chloride solutions (23%) is given as -6°F while the corresponding value for the magnesium chloride solution (21%) is -22°F. The eutectic temperature for calcium chloride solutions (30%) is -50°F. However -40°F is about the lowest practical operating temperature, since the brine solutions have a tendency to precipitate solid salt if the concentration approaches the eutectic value. This precipitated solid will clog pipes and pumps with a subsequent decrease in heat transfer.

A very serious shortcoming of the low cost brines is their corrosive action on metals due to the electrolytic nature of their aqueous solutions. Both calcium and magnesium chlorides undergo hydrolysis resulting in an acid reaction, which increases the corrosiveness of these salts. Further, unless soft water is employed in the preparation of the calcium brines, a precipitate will be formed by components of hard water. While sodium chloride does not hydrolyze, it is a highly corrosive material. The brines may be inhibited to reduce their corrosive nature, but in spite of every known method of inhibition, they still present very serious corrosion problems. Sodium dichromate is commonly employed as a brine inhibitor. Also, inorganic phosphate salts such as disodium phosphate, tripolyphosphate, trisodium phosphate, have been used as inhibitors. In general, chemical inhibitors have been ineffective in decreasing the corrosion of brine solutions on the common metals.

The most useful antifreeze agents consist of organic compounds such as mono-, di-, and polyhydroxy derivatives. In general, these materials are flammable or combustible by contrast with the nonflammable inorganic salts. However, aqueous solutions of the higher boiling compounds are nonflammable at normal operating temperatures.

Mixtures boiling lower than water tend to lose the antifreeze agents when subject to overheating in a given system, while the polyhydroxy (glycols and glycerine) solutions will lose water rather than the antifreeze material. Therefore, aqueous solutions of high boiling compounds (above 212°F) will be retained in the system since the antifreeze agent is not lost by evaporation. Inasmuch as the eutectic points for these polyhydroxy compounds are much lower than for brine solutions, they are useful at lower temperatures as indicated in the following table:

OPERABLE TEMPERATURES FOR VARIOUS HYDROXY ANTIFREEZE AGENTS

	Minimum Operable Temperature	Antifreeze Concentration
Methanol	-54°F	50% (by volume)
Ethanol	-50	72
Isopropanol	-50	81
Ethylene glycol	-56	58
Propylene glycol	-32	52
Glycerine	-12	65

The effectiveness of a specific antifreeze agent is inversely related to its molecular weight, since the lowering of the freezing point of water is determined by the number of moles of antifreeze agent present in a given solution. Below are listed the molecular weights of a number of compounds as well as the concentration needed to lower the freezing point of water solutions to 0°F. These data rate the several antifreeze agents as to their ability to lower the freezing point of water.

MOLECULAR WEIGHTS OF HYDROXY COMPOUNDS AND CONCENTRATIONS FOR 0°F PROTECTION

	M W.	Concentration to Protect to 0°F
Methanol	32	27% (by volume)
Ethanol	46	31
Isopropanol	60	42
Ethylene glycol	62	33
Propylene glycol	76	36
Glycerine	92	42
Cane sugar	342	75

It is evident from the above data that methanol is the most effective freezing point depressant, while cane sugar is least efficient. Actually, cane sugar, honey, glucose, etc., are not suitable antifreeze agents since they require such high concentrations to reduce the freezing point of water that the solutions are too viscous.

The hydroxy compound types of antifreeze agents have the further advantage of being relatively noncorrosive to the common metals. Further, their solutions will not precipitate crystalline salt deposits at low temperatures. These solutions may be pumped through pipes at temperatures somewhat below the freezing point without mechanical damage to the system. Certain glycol solutions can be pumped at temperatures of 10°F below their freezing point.

Selection and Use of Antifreeze. During the period of normal supply both types of antifreezes (methanol and ethylene glycol) are readily avail-

able. Both may be employed under average driving conditions. However, the nonvolatile type is recommended to meet variable driving conditions, such as heavy loads, long periods of idling and high altitudes. The average motorist selects the glycol antifreeze to insure against freezing throughout the winter season regardless of weather and driving conditions.

Sufficient antifreeze should be added to protect the cooling system to about 15°F below the average annual minimum temperature. If an unusually low temperature develops, the freezing point of the radiator solution should be checked and additional antifreeze added, if needed. The concentration of antifreeze in the radiator is determined by a specific gravity hydrometer. Since the specific gravity of the aqueous antifreeze solution varies with the concentration, charts giving the freezing points as a function of the concentration are available for volatile and nonvolatile (permanent) products. Mixtures of alcohol and glycol antifreezes cannot be checked by a hydrometer since the specific gravity of the two antifreeze types differs widely.

Antifreeze Inhibitors. Uninhibited water is corrosive to metals of the cooling system. This corrosive action exhibits itself in aqueous antifreeze solutions and inhibitors are therefore incorporated in the concentrated antifreeze. Indeed, this is the reason for the recommendation of all antifreeze manufacturers to inhibit water used in coolant systems during the summer months. Much experimental work has been done to minimize the corrosion characteristics of aqueous solution of antifreezes. In general, about 1-3% of a compounded antifreeze is corrosion inhibitors. These additives may be of an organic or inorganic nature. The several antifreeze manufacturers have developed inhibitor combinations which will maintain the corrosion tendency at a minimum. Since each manufacturer develops a specific inhibitor for his product, it is not advisable to mix two types of antifreezes because the inhibitor blends may tend to nullify each other.

For the nonvolatile product there are two general types of inhibitor systems, single and two phase. The volatile products are usually produced in a single phase form, although in some a second phase may result upon dilutions with water. The mono-phase type of inhibitor, which is completely soluble in the glycol or alcohol, consists of such compounds as borates, phosphates, nitrites, tungstates, molybdates, amines and amine salts. In general, these compounds protect the metal surfaces through the formation of a protective film. A two phase inhibitor system usually contains an oil phase of about 1-2% by volume, and consists of sulfonated oil, animal or vegetable oils or derivatives. These materials protect the metallic surfaces by coating them with an oil film, although there is always the possibility that the film may not be uniformly distributed throughout the cooling system.

Other Applications of Antifreeze Agents. Brine solutions are still frequently used as refrigerants in plant processing. Hydroxy compounds (glycols) are also employed for the same purpose

to avoid corrosion. In food-processing plants such as dairies, breweries, and packaging plants, inhibited propylene glycol is used because of its very low toxicity. An inhibited glycol solution is also used to remove ice formed by passage of moisture over cooling coils of large industrial air-conditioning units. Antifreeze agents are incorporated in formulations to prevent freezing and possible destruction of emulsions used in pharmaceutical and cosmetic creams. Glycol is also added to cement to prevent cracking during the winter.

Aqueous types of nonflammable industrial hydraulic fluids utilize glycols as freezing point depressants for the water component. These fluids are used in the operation of hydraulic lifts, die casting machines, ingot manipulators, etc.

A number of deicing formulations have been developed for the removal of ice and frost from such exposed surfaces of aircraft as leading edges of the wings, fuselage, etc. They consist of inhibited alcohol or inhibited alcohol glycol combinations. This problem has become more acute with the advent of long flights at high altitudes when humidity may vary through a wide range. The deicing fluid should not only melt ice, but also prevent its formation for several hours. These deicing fluids consist of a blend of glycol and inorganic salts.

In hydraulic fluids there is also an antifreeze problem. For many years, the Naval Bureau of Aeronautics has used a nonflammable aqueous type hydraulic fluid for their fighter planes. A similar fluid operates the catapult mechanisms on the aircraft carriers. In both these applications a glycol is incorporated in the product to lower the freezing point.

Deicing fluids have been used to remove ice from automotive windshields. They consisted of aqueous solutions of isopropyl alcohol, alcohol glycol combination, and glycerine. In recent years antifreeze compounds have been added to the gasoline to prevent freezing of condensed moisture during the winter months. Isopropyl and methyl alcohols have been employed for this purpose. Recently petroleum producers have been adding isopropyl alcohol to the gasoline at the refinery for the same purpose.

A number of cities have used sodium or calcium chloride to melt the ice and snow in city streets. These salts are very effective as deicers but are highly corrosive to the vehicles. The addition of chemical inhibitors has not proved to be effective in controlling the corrosive action of the salt on metal surfaces.

CHESTER M. WHITE

Cross-references: *Heat Transfer, Eutectic, Additives, Solutions, Alcohols*

ANTIKNOCK AGENTS

An antiknock agent is a chemical which, when added in small amounts to gasoline, raises its octane number. Many compounds possess this property to varying degrees, but they are all compounds of rather few elements. Except for nitrogen compounds, the antiknock effect is almost directly

related to the atomic concentration of the effective element, the nature of the compound in which it is present having only secondary significance, such as to make the material soluble in gasoline and sufficiently volatile for induction through a carburetor.

The main antiknock agents are compounds of nitrogen (as aromatic amines only), iodine (elemental or combined), and some metallic or semi-metallic elements. The most significant ones are listed below together with their relative effectiveness, on an atom basis.

RELATIVE EFFECTIVENESS OF ANTIKNOCK AGENTS
(Reciprocal of number of moles giving the same antiknock effect as 1 mole of aniline)

Aniline	1 0
Ethyl iodide	1.1
Titanium tetrachloride	3 2
Tetraethyltin	4.0
Diethylselenium	6 9
Triethylbismuth	24
Diethyltellurium	27
Nickel carbonyl	35
Iron carbonyl	50
Tetraethyllead	118

Other aromatic amines vary in effectiveness from 0.2 to 1.5 compared to aniline, while nitrogen in other forms is ineffective. Other organolead compounds differ very little from tetraethyllead (TEL), as long as they are soluble in gasoline and somewhat volatile.

The best materials, iron carbonyl and tetraethyllead, show a potency of 50 and 100 fold that of aniline, respectively. These figures are only approximate, because they vary not only with the gasoline used but also with the engine operating conditions and with the concentration of antiknock agents. In general, the octane number (O.N.) of a gasoline will be raised about 10 O.N. with 1.0 ml of TEL added to one U. S. gallon of fuel, and 20 O.N. with 3.0 ml.

Iron carbonyl, while the least expensive on the basis of cost and effectiveness, never gained wide use, because the iron oxides formed by its combustion cause excessive engine wear and shortens the life of the spark plugs.

Tetraethyllead has been in commercial use since 1925, and is now used in many countries; it is a component of practically all aviation and automotive fuels in the United States. In order to avoid the formation during its combustion of objectionable lead oxide, it is added to gasoline in admixtures with ethylene bromide, with or without the further admixture of ethylene chloride. When the former is used alone, the proportions are mole-to-mole (one theory), to lead to the formation of lead bromide. When $C_2H_4Cl_2$ and $C_2H_4Br_2$ are used together, the "theory" of bromine is reduced by not more than 0.5, and about twice as much chlorine is used instead, such, for instance, as in 0.85 theory Br + 0.30 theory Cl.

Pure TEL, and also its concentrated mixtures with $C_2H_4Br_2$ and $C_2H_4Cl_2$, are hazardous to handle, and therefore the antiknock agent is blended at the refineries under safe conditions.

The leaded gasoline is safe to handle as a motor fuel, but should not be used for washing purposes or other forms of direct skin contact.

The decrease in antiknock effectiveness with increase in concentration makes it inadvisable to use over 6 ml TEL per gallon for aviation fuel; for motor fuel the concentration is limited, for economic reasons as well as for safety, to 3.0 ml per gallon.

Regular and premium grade motor gasolines in the United States contain on the average about 2 ml TEL per gallon. The total consumption of TEL in the United States in 1955 amounted to several hundred thousand tons.

The presence of TEL in gasoline can be detected by shaking a small sample of the gasoline with concentrated HCl and testing for lead in the aqueous layer. For quantitative determination 50 or 100 ml of gasoline is refluxed for 30 min. with an equal volume of concentrated HCl. The aqueous layer and washings are evaporated to dryness and the residue is analyzed for lead.

GEORGE CALINGAERT

Cross-references: *Additives, Gasoline, Organo-metallic Compounds*

ANTIMONY

Antimony, symbol Sb (L. *stibium*), is a hard, brittle, silver white metal of atomic number 51 and atomic weight 121.76. It is located in Group V A of the Periodic Table with nitrogen, phosphorus, arsenic and bismuth, and has been known since earliest times in the form of compounds and alloys. Although native antimony has been found in isolated instances, the metal and its compounds are derived from ores, the chief of which is stibnite or antimony glance, Sb_2S_3 ; other minerals are antimonides and sulfantimonides of other metals, frequently associated with mercury, silver, lead and copper ores. While antimony is 58th in order of occurrence of the elements in the earth's crust, it is relatively common because it is derived largely as a by product in the production of lead and copper.

The metal is extracted from its sulfide ores by roasting to convert it to the volatile oxide, which is then reduced with carbon, or by reduction with scrap iron in the presence of a salt or sodium sulfate slagging agent. Much antimony is recovered as a lead alloy, especially the secondary metal derived from scrap. In 1953 the United States consumption was 39,100 tons, comprised of 14,300 tons of primary metal (chiefly from Bolivian and Mexican ores), 2,800 tons contained in lead-silver ore consumed in the manufacture of antimonial lead, and 22,000 tons of secondary metal almost entirely as a lead alloy from scrap storage batteries. The current price of antimony is 33.5¢ per pound, less than that of copper (1955).

The physical properties of antimony include: density, 6.684 g/cc; melting point, 630.5°C; boiling point, 1440°C; specific heat, 0.0504 cal/g°C (20°-100°C); latent heat of fusion, 38.3 cal/g; latent heat of vaporization, 383 cal/g; coefficient of thermal expansion, 8.5 to 10.8×10^{-6} (20°C), depending

upon the crystal orientation; electrical resistivity, 41.7 microhm-cm (20°C); vapor pressure, $\log_{10}P$ (mm Hg) = $-9871.5/T + 9.051$ (range 1070°–1325°C), where $T = ^\circ\text{K}$; thermal conductivity 0.045 cal/sec/cm²/°C/cm (25°C); surface tension, 383 dynes/cm (635°C) in H_2 ; modulus of elasticity 11.3×10^6 psi; hardness 42 Brinell; thermal neutron absorption cross section, 5 barns. Antimony crystallizes in the stable rhombohedral system, and two other allotropic forms are known. Isotopes are 121 and 123 in the relative amounts of 56 and 44.

Antimony is not attacked by air or oxygen at ordinary temperatures, but when heated is converted to the trioxide. Water reacts with it at elevated temperatures, and it burns in chlorine to yield antimony trichloride, SbCl_3 . Antimony is not attacked by hydrofluoric acid nor by dilute hydrochloric or sulfuric acids, but is dissolved by concentrated HCl and H_2SO_4 , forming, respectively, SbCl_3 and unstable $\text{Sb}_2(\text{SO}_4)_3$. Nitric acid oxidizes the metal. It combines directly with sulfur, phosphorus, arsenic, tellurium, selenium, and with many metals, such as sodium and lead, to form definite compounds. Carbon, silicon, boron and nitrogen do not react with antimony.

Antimony, like arsenic and bismuth, forms trivalent and pentavalent compounds, the former being the more common. All of the halogen compounds, except SbBr_3 , are known at both valence levels. Most of them are hydrolyzed by water to form oxy compounds, such as Sb_2O_3 from SbCl_3 and hot water. Antimony hydride, SbH_3 , formed by the action of HCl or H_2SO_4 on a zinc-antimony alloy, is a colorless, poisonous gas with a garlic-like odor. Two series of oxygen acids or salts are known: H_3SbO_3 , orthoantimonous acid, and H_5SbO_4 , orthoantimonic acid which on heating passes into H_3SbO_7 , pyroantimonic acid. Tartar emetic, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, an important commercial antimony salt, is formed by boiling a solution of potassium hydrogen tartrate, "cream of tartar," with antimony trioxide.

In the United States almost 80 per cent of the total primary and secondary antimony is consumed in the form of alloys, chiefly those of lead for battery plates (9 per cent Sb, the largest single use of antimony as well as of lead), cable coverings (1 per cent Sb), sheet and pipe (6 per cent Sb), and castings (10 per cent Sb); in all these uses it increases the hardness and strength of lead. It is a vital component of tin and lead alloys for bearings, solders and type metal. Antimony is classed as a strategic material.

The other 20 per cent, some 8300 tons in 1952, is consumed as antimony chemicals. Sb_2O_3 , m.p. 656°C, is a pigment in paints, enamels and glass, and finds an important use in flameproofing textiles. SbCl_3 , m.p. 73.4°C, and SbCl_5 , b.p. 140°C, are chlorinating agents in organic syntheses. SbF_3 , m.p. 202°C, is used in procelain, in dyeing, and as a fluorinating agent. Sb_2S_3 is used in rubber vulcanization. Sb_2S_3 , m.p. 546°C, is a constituent of matches, percussion caps and pyrotechnics, and is a paint and glass pigment; as a valuable component of camouflage paints its property of reflecting infrared rays is similar to that of green

vegetation. Antimony compounds, chiefly organic, are applied in medicine as diaphoretics, febrifuges, parasiticides and emetics. Antimony metal is non-toxic, but its soluble compounds are poisonous although lower in toxicity than those of arsenic.

CLIFFORD A. HAMPEL

ANTIOXIDANTS

For Rubbers

Rubbers, both natural and synthetic, undergo gradual deterioration during aging, as a result of the combined effects of heat, light, oxygen and ozone. While materials which impart improved aging properties of any kind to rubbers, are often termed age resisters, this term is also sometimes used to cover a specific condition, for example flex cracking, oxidation, deterioration due to prolonged heating, etc. Materials which retard absorption of oxygen or the effects of oxidation on natural rubber are commonly called *antioxidants*. Raw natural rubber contains natural substances which behave as antioxidants, and impart satisfactory protection to the polymer in the unvulcanized state. Synthetic rubbers must be protected against oxidation at the time of manufacture by addition of materials called stabilizers which function as antioxidants in natural rubber. In modern commercial practice the term "antioxidant" refers to a material which is essentially without effect on the rate of vulcanization, but which retards the deterioration of elastic properties caused by oxidation.

CHEMICAL CLASSIFICATION OF ANTIOXIDANTS

Classification	Examples
Secondary arylamines	N,N' Diphenyl- <i>p</i> phenylene diamine N-Phenyl 2-naphthylamine Diocetyl diphenylamine
Alkylarylamine	N,N' Diphenylethylenediamine
Ketone-amine	Acetone diphenylamine reaction product
Alkylated phenols	2,6 Di- <i>tert.</i> butyl-4-methyl phenol 2,2 Methylenebis (4 methyl-6- <i>tert.</i> -butylphenol) Styrene-phenol reaction product
Phosphite ester	Trinonylphenyl Phosphite
Alkylated phenolsulfide	1,4-Thiobis (6- <i>tert.</i> -butyl-3-methylphenol)
Dihydroquinolines	2,2,4 Trimethyl-1,2-dihydroquinoline 2,2,4 Trimethyl-6-phenyl-1,2-dihydroquinoline

Unvulcanized natural rubber does not undergo serious deterioration under ordinary conditions of production or storage. However, after vulcanization, the finished rubber article is susceptible to oxidation, with the result that its elastic properties are gradually destroyed. Antioxidants are therefore usually added before vulcanization to minimize the effect of oxidation. Since unvulcan-

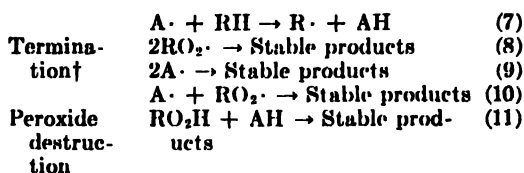
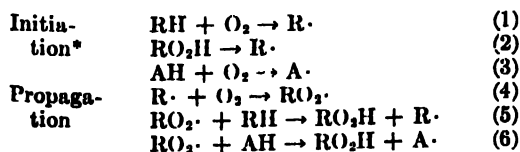
ized synthetic rubbers are susceptible to oxidation, an antioxidant is added at the time of manufacture of the rubber, which serves to protect against oxidation after the rubber is vulcanized. Antioxidants are normally added to elastomers in an amount varying from about 0.15 to 3 parts per hundred parts of elastomer. Commercial antioxidants may be divided into two classes depending on whether they discolor when exposed to light. Those which neither discolor in light nor stain other materials in direct contact are called nonstaining, nondiscoloring antioxidants, and are used in light-colored rubber articles. Those which discolor in light are referred to as staining antioxidants. Most of these are derivatives of aromatic amines or the reaction product of an aldehyde or ketone with an aromatic amine. Nonstaining antioxidants are usually hindered phenols or derivatives of aromatic phosphite esters.

For commercial use it is desirable that an antioxidant be odorless, tasteless, nontoxic and non-irritating to the skin. It should be in a form which permits ready dispersion in rubber and should not bloom to the surface due to limited solubility. Prices of commercial antioxidants range from about \$0.50 to \$3 per pound. The total production of antioxidants in 1952 was 48,000,000 pounds.

Antioxidant efficiency is evaluated in the laboratory by comparative tests in which either the absorption of oxygen or the deterioration of physical properties such as tensile strength, flex life, etc., is measured. When vulcanized natural rubber has absorbed about 1 per cent or more of oxygen its useful properties have practically disappeared. For evaluation purposes, acceleration of the aging process is usually achieved by increasing the temperature and the oxygen pressure (oxygen bomb test). Antioxidants efficiently retard oxidation in the dark but are of little value in protecting against light-catalyzed oxidation.

It has been recognized for some time that antioxidants function by exerting some form of negative catalysis rather than by selective reaction with oxygen. Present theories of the mechanism are based largely on the assumption that the oxidation process in elastomers is analogous to the well established mechanism for oxidation of olefinic hydrocarbons. Additional evidence in support of this theory is necessary, since it is known that in the important case of sulfurated hydrocarbons (vulcanized rubbers) containing carbon black, factors are present which may alter this mechanism.

It is generally accepted that oxidation of hydrocarbons proceeds by a free radical chain mechanism. In the mechanism outlined below the symbol RII represents the olefin with an α -methylene hydrogen atom, H. The primary reaction product, a hydroperoxide, is represented by RO_2H , and an antioxidant by the symbol AH



* Reactions (1) and (2) are the overall result of one or more successive reactions.

† Under conditions where $(R\cdot) \ll (RO_2\cdot)$.

Phenolic antioxidants are believed to function by reacting with the $RO_2\cdot$ radical as indicated by reaction (6). The radical $A\cdot$, derived from the phenolic antioxidant, is either incapable of propagating the chain via reaction (7) or propagates the reaction with very low efficiency. The rate of oxidation is reduced because the length of the chain reaction is reduced.

The behavior of amine antioxidants is probably more complex. One effect of an amine antioxidant is probably to reduce the initiation of reaction chains via reaction (2) by converting the peroxide to a stable product without formation of free radicals. The radical $A\cdot$, formed from an amine antioxidant via reactions (3) and (6), is believed to be capable of propagating the chain reaction, but probably with lower efficiency than the $RO_2\cdot$ radical. This would tend to reduce the oxidation rate. Reaction (3) will increase the oxidation rate regardless of the efficiency of radical $A\cdot$ in propagating the chain. The overall effect of an amine antioxidant on the oxidation rate will depend on the magnitude of the opposing effects.

Some antioxidants, which efficiently retard oxidation in the dark, accelerate oxidation in light. This effect is probably due to the formation of chain initiating radicals by the action of light on the antioxidant. An additional factor which may reduce the effectiveness of an antioxidant in protecting against light-catalyzed oxidation is the probability that the kinetic chain length is shorter for photo-oxidation than for thermal oxidation.

R. P. DINSMORE

Cross-references: Additives, Antiozonants, Rubber, Oxidation, Amines, Autoxidation

For Lubricants

Since almost all lubricants consist wholly or in large part of organic compounds, they oxidize in the presence of air. This oxidation results in deterioration of the lubricant with a marked change in viscosity (usually an increase), the precipitation of insoluble materials and/or the corrosion of metal parts in contact with the lubricant. Small amounts of certain additives, known as antioxidants or inhibitors, greatly decrease the rate of oxidative deterioration. The amount added usually lies between 0.01 and 3 per cent, depending on the antioxidant used. The total amount of lubricant antioxidants used in the United States in one month is about twelve million pounds.

Most lubricant antioxidants fall into the following classes: (1) aromatic amines, (2) phenols, (3) compounds containing sulfur or selenium, (4) compounds containing phosphorus. Phenyl- α -

naphthylamine, alkylated diphenylamines and unsymmetrical diphenylhydrazine are typical amine type antioxidants. Tetramethyldiaminodiphenylmethane is an effective antioxidant at temperatures above 100°C where many other amines are ineffective. Among the phenolic compounds, hydroquinone, β -naphthol and alizarin show inhibitory action. However, the most commonly used antioxidants are substitution derivatives of phenol, such as 2,6-di-*tert* butyl-*p*-cresol, *o*-cyclohexylphenol, and *p*-phenylphenol.

Lubricating oil containing a small amount of dissolved sulfur is effectively inhibited, but is quite corrosive toward copper and its alloys. However, if an organic compound of sulfur is added, inhibition may be achieved without corrosion. Suitable compounds can be produced by reacting sulfur with unsaturated esters such as sperm oil, or with other unsaturated organic compounds such as terpenes and polybutenes. Similar compounds may also be prepared by the reaction of chlorinated wax with sodium sulfide. The products of these reactions are complex, and the sulfur is present in a number of forms such as sulfides, disulfides, etc. Aromatic and aliphatic sulfides, such as dibenzyl sulfide and alkylated diphenyl sulfide, are sometimes used.

Some selenium derivatives are also excellent antioxidants. Diethyl selenide gives much greater inhibition than the corresponding sulfur compound. Dilauryl selenide is particularly useful for temperatures above 100°C.

Like sulfur, elementary phosphorus is an effective antioxidant, but is too corrosive for actual application. The most common phosphorus containing antioxidants are alkyl and aryl phosphites such as tributyl phosphite and tris (*p*-*tert*-amyl phenyl) phosphite. Naturally occurring phosphorus compounds such as lecithin are also used.

Compounds containing both sulfur and phosphorus have been used extensively as antioxidants. In general, inhibitors containing both elements are definitely superior to those containing only one. Most of the phosphorus-sulfur inhibitors are produced by the reaction of high molecular weight alcohols or unsaturated organic compounds with phosphorus pentasulfide. The alcohols (such as lauryl alcohol, cyclohexanol or butyl phenol) yield dithiophosphoric acids, which are used in the form of their barium, calcium or zinc salts. Phosphorus pentasulfide reacts with terpenes, polybutenes, unsaturated fatty acids and esters, and so forth to give an almost unlimited number of complex addition products.

There are also some organic compounds containing sulfur and nitrogen which are excellent antioxidants. A number of polyvalent metal dithiocarbamates give good inhibition. Phenothiazine is at present the antioxidant most generally employed in diester synthetic oils.

Naturally, the effect of any antioxidant will vary greatly with the nature of the lubricant in which it is used.

Since autoxidation apparently proceeds by a free radical chain mechanism, antioxidants are considered to function by breaking the chain. Thus, the reaction of one molecule of antioxidant

with a chain carrier serves to prevent the oxidation of hundreds or even thousands of lubricant molecules. When the inhibitor reacts, it may be oxidized to a compound which no longer will inhibit oxidation, it may be oxidized to a compound which is a less potent antioxidant, or it may be regenerated. The latter type is, of course, the most desirable. Phenothiazine apparently owes its great inhibitory power to a regenerative reaction which converts active peroxide oxygen to a less active form.

ALAN DOBRY

Cross-references: *Additives, Lubricating Oils*

For Food Products

Antioxidants are chemical compounds which retard oxidation and thus increase the shelf life of foods. Nature was the first to use antioxidants in her storage problems. The tocopherols occur in many fruits, nuts, vegetables, and meats where they may prevent oxidation. Hog fats contain from 1 to 3 parts of tocopherols per 100,000, while the vegetable fats contain from 30 to 100 parts per 100,000. The addition of from 1 to 10 per cent of certain vegetable fats to lard increases the stability of the lard three- to five fold. The preserving action of the spices, especially rosemary and sage, may be explained by the antioxygenic activity they possess. Preservation of meat by smoking is known to be due to the aromatic compounds in the smoke. Another natural product, ascorbic acid, has been claimed to have antioxygenic activity, but this effect has not been well established. The use of natural and artificial antioxidants has increased materially since the Food and Drug Administration (FDA) has permitted the addition of certain compounds to certain foods. As a rule the most powerful antioxidants are phenolic compounds such as hydroquinone, nordihydroguaiaretic acid (NDGA), butylated hydroxyanisole (BHA), noreconidendrin, gum guaiac, and the tocopherols.

Synergists have no antioxygenic value in themselves, but they increase the effectiveness of any natural or artificial antioxidants in the food. Certain acids are known to act in this capacity. Ascorbic, citric and phosphoric acids, the monoesters of ascorbic and fatty acid esters of citric acid, are frequently used as synergists. Ascorbic acid may retard oxidation slightly because it is a reducing agent which may consume part of the dissolved oxygen or reduce the oxidation-reduction potential. Certain compounds such as citric acid and sorbitol act as chelating agents for the removal of metals, such as copper and iron, which promote oxidation.

The concentration of antioxidants approved by the FDA varies with the product but the maximum is 0.02 per cent. Some compounds are effective in concentrations as low as 0.0025 per cent. Any food product containing an added antioxidant must be so labeled.

Some antioxidants have certain properties not possessed by the others. For example, BHA and gum guaiac carry through the heat treatment of baking better than some of the others. Because of

the difference in properties, mixtures of antioxidants and synergists are often used.

The prevention of oxidation in animal products such as fish, meats, and poultry, is of great economic importance, but unfortunately success in this field has been limited, probably because of the poor contact of the antioxidant with the fat and the presence of moisture. The oxidative discoloration of many fruits and vegetables has been retarded by treatment with ascorbic acid. This compound may play three roles in retarding oxidation. They are its action as a reducing agent, acid, and synergist. The discoloration of canned mushrooms has been reduced and the flavor improved by the addition of ascorbic and citric acids.

Antioxidants are used to prevent oxidation of the vitamins. α -Tocopherol (vitamin E) and ascorbic acid (vitamin C) are often added to prevent oxidation of vitamin A.

New antioxidants are being tailor-made to meet certain problems in food preservation.

GEORGE R. GREENBANK

Cross-references: Additives, Foods, Oxidation

ANTIOZONANTS

Antiozonants, sometimes referred to as "antioxidants" and as "sunproofing agents," impart to natural rubber and synthetic rubber compounds various degrees of resistance to atmospheric ozone. The cracking of rubber on exposure to the atmosphere is caused by two separate mechanisms. Light activated oxidation results in a resinification of the surface; the surface, being brittle, breaks in an irregular cross pattern as a result of surface shrinkage or movement caused by contraction and expansion or other disturbances. The second mechanism is the attack of ozone on strained rubber which takes place in the dark as well as in light and results in cracks running at right angles to the strain. A complex strain pattern will result in a complex crack pattern, but cracking resulting from ozone can usually be identified as being distinct from cracking due to light-activated oxidation.

The atmospheric ozone effect is very often visible in a matter of days, and severe, damaging cracks may develop in weeks. Its action is progressive and once started is not reduced or halted until stress relaxation occurs or the ozone concentration is reduced.

The light-activated oxidation effect is a surface effect which tends to lend protection to the underlying material and is often not particularly disruptive of the rubber's useful life, providing that the article is not thin in cross-section and a high ratio of volume to surface exists.

Petroleum waxes have come to be known as "sunproofing agents" because the cracks in rubber caused by ozone were formerly considered by many to result from exposure of rubber to the sun, and the addition of waxes to rubber compounds tends to reduce or prevent this type of cracking. Waxes are often still referred to in this manner. They function by being incorporated in the rubber in amounts exceeding their solubilities in the

compound so that they migrate to the surface (bloom). This surface layer prevents the ozone from contacting the rubber and thus ozone cracking does not result. A small amount of wax may be more harmful than beneficial, as the surface is spottily coated with wax and where the wax is thin or missing, ozone attack results in large, deep cracks. With no wax, the surface is often uniformly covered with small, shallow cracks which stress-relieve the surface as they form. Wax blooms are often protective for static exposure but if such blooms are lacking in adhesion or flexibility, they will rupture or break away from the rubber surface during dynamic use. This again results in larger and deeper cracks than if no wax had been incorporated.

Waxes used for imparting ozone protection are usually mixtures of microcrystalline and amorphous waxes, some of which are designed to form flexible blooms at winter atmospheric temperatures and yet produce sufficient blooms at the higher temperatures of summer. As temperature rises, the solubility of waxes in polymers increases and thus less wax is available to form the protective bloom. Higher quantities of wax generally help at elevated temperatures, but they may form heavy, crusty, undesirable blooms at normal room temperatures. Paraffin is often effective, but paraffin blooms are generally brittle.

Certain antioxidants, often of the type which provide resistance to flex cracking, also impart added ozone resistance. Some of these antioxidants, when used as antiozonants, must be used in concentrations as high as five parts on the rubber. Often some wax is desirable in the compound to assist in carrying the antiozonant to the rubber surface. Some of these materials also impart dynamic protection which is of concern in such things as tire sidewalls. Representative materials are: (1) secondary aromatic amines such as *N,N'*-diethyl-paraphenylenediamine and diphenyl-paraphenylenediamine, and (2) quinoline derivatives such as 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and polymerized 1,2-dihydro-2,2,4-trimethylquinoline.

Certain furane derivatives have also been shown to have antiozonant properties; and for many years it has been known that vulcanized oils, generally known as factice, when used in relatively high loadings, impart ozone resistance, but at the expense of lowering most physical properties. All the materials referred to above are properly called antiozonants as they protect from ozone, as already described.

Reduction of light-activated oxidation effects can be obtained in two ways. Incorporation of opaque ingredients in the rubber will lessen penetration of ultraviolet energy into the rubber and thus reduce the thickness of the oxidized layer. Carbon blacks, certain colors and titanium dioxide act as light shields in this manner. Black compounds resist light-activated oxidation fairly well, but nonblack compounds will generally surface deteriorate on exposure. The incorporation of antioxidants in rubber compounds will reduce light-activated oxidation effects to some extent. The use of nickel dibutyl dithiocarbamate appears

helpful in nonblack neoprene compounds for reducing and delaying the formation of an oxidized skin.

C. V. LUNDBERG

Cross-references: *Antioxidants, Waxes*

ANTISEPTICS

Antiseptics are chemical substances which kill or prevent the growth of microorganisms when applied to living tissue. Iodine and certain chlorine compounds are widely used as antiseptics. Iodine has been used for the purpose since 1839 and in surgery since 1862. The common forms are: Iodine Tincture, U.S.P., (since 1840) consists of 2.0% I, and 2.4% NaI in alcohol (U.S.P. XV); Iodine Tincture, Strong, N.F., 7% I and 5.0% KI in alcohol; Iodine Solution, N.F., 2.0% I and 2.4% NaI in H₂O. The best is the tincture which penetrates rapidly, is highly germicidal, nonspecific, and is not counteracted by organic matter. Chlorine compounds, counteracted to variable extents by organic matter, include sodium hypochlorite (Dakin's solution), dichloramine-T, etc. Fluorine and bromine are effective but not used.

Mercuric chloride has been widely used since 1881, but has been largely replaced by less toxic compounds, whereas mercurous chloride, mercury oxycyanide, mercury cyanide, and potassium mercuric iodide have only limited use. These compounds are bacteriostatic in high dilution, germicidal in much greater concentrations, but counteracted to a large extent by organic matter. Organic mercury compounds are far less toxic, nonirritating, and are highly bacteriostatic, germicidal, and nonspecific, but are counteracted to variable degrees by organic matter; the most important are merphenyl nitrate, Merthiolate, Methaphen, Mercurochrome, and Mercresin.

The most widely used silver compounds are Silver Nitrate, U.S.P., Ammoniacal Silver Nitrate Solution, N.F., silver picrate, N.N.R., and certain colloidal silver preparations such as Strong Protein Silver, N.F., Mild Silver Protein, U.S.P. (Argyrol), etc., all of which are effective germicides of low toxicity; they are used extensively on mucous membranes and they are not counteracted by organic matter.

Bis-phenols are highly bacteriostatic and fungistatic and are widely used for the purpose, especially in soaps and detergents, mildew-preventing formulations, etc., the halogenated form being most commonly employed, such as dichlorophene, tetrachlorophene, hexachlorophene, and bithionol. The germicidal properties are considerably reduced in the presence of organic matter. When used repeatedly on the skin, as in soaps and detergents, they have a tendency to remain for long periods, thus reducing skin bacteria to a significant degree, hence valuable in preoperative hand washing.

While phenol was the first widely used antiseptic, employed from 1865 to 1880 and later, it has been largely replaced because of its highly toxic property. Certain compounds, such as Saponated Cresol Solution, N.F., and halogenated

phenol derivatives and others, are effective for the purpose, are less toxic and are not counteracted appreciably by organic matter.

Many organic pentavalent nitrogen compounds (quaternary ammonium compounds) are germicides. While these are used primarily as disinfectants, a few are employed as antiseptics, such as in Zephiran, Cepacrol, etc. They are effective for the purpose in proper concentration, but are counteracted to an appreciable extent by organic matter, especially by blood serum. They are, however, nontoxic and nonirritating, and may be used in the place of alcohol following pre-operative scrub-up.

Essential oils both natural and synthetic have long been used as antiseptics and are still widely employed. The most important are thymol, eucalyptol, menthol, bergamot, etc. In the concentrations used these oils are effectively germicidal, nontoxic, nonirritating, agreeable as to taste and odor, and not counteracted by organic matter.

Used effectively since 1894, alcohols are still widely employed as antiseptics. Ethyl alcohol in 62.5% to 70% concentration is most commonly used. It is rapidly germicidal, but weakly bacteriostatic in higher dilution, is nontoxic, nonirritating, and not counteracted by organic matter, it is widely used for degreasing the skin. Isopropyl alcohol is equal if not superior to ethyl alcohol, but methyl alcohol is much weaker.

For certain purposes oxidizing compounds are effective antiseptics. The most important are hydrogen peroxide, zinc peroxide, potassium permanganate, sodium perborate, and glycerite of peroxide. Because of danger associated with the use of these compounds, they are usually employed for special purposes, especially where large amounts of organic matter are not present.

Bacteriostatic dyes have limited and special uses in surgery and are not ordinarily employed otherwise. They are selective in their activity and are used to prevent the growth of specific kinds or classes of bacteria; they are also to some extent toxic to tissue, but not appreciably affected by organic matter. The most important are crystal violet, acriflavine, methylene blue, and the pyridine compounds.

It is quite impossible to evaluate the relative effectiveness of various antiseptics since they vary in their efficiency under different conditions of use, that is, some are more suitable for certain purposes than others regardless of their respective germicidal or bacteriostatic properties.

G. F. REDDISH

APPERT, FRANCOIS (1750-1840)

Born in Châlons-sur-Marne, France. In 1795, Napoleon offered a prize for a process of food preservation, which stimulated Appert to investigate the problem. Appert was a self-educated man who described himself as "an old confectioner and distiller", a chef, and altogether broadly experienced in handling foods. In 1810 he published his famous treatise "L'art de conserver pendant

plusieurs années toutes les substances animales et végétales". This work describes for the first time a successful method of preserving foods, without the use of chemicals or drying, simply by subjecting them to prolonged boiling and then hermetically sealing them. However, Appert did not know the words "canning" or "tinning", conserving the heat-sterilized foods in glass jars sealed with cork. His process was fundamentally similar to home canning. Somewhat later the English inventor, Peter Durand, initiated the use of tin-lined containers (now tins or cans) and M. Raymond Chevallier-Appert introduced the essential improvement of sterilizing the foods by boiling them under elevated pressures (autoclaving them) before sealing. Thus began the great canning industry.

BERNARD JAFFE

ARCHAEOLOGICAL CHEMISTRY

The most obvious and frequent application of chemistry to archaeology is the exact identification of materials found in excavations. Errors of identification, some of them rather glaring from the chemical viewpoint, are rather frequent in the older archaeological literature and are by no means absent from some of the more recent literature. Such confusions have arisen either because no correct identification was made in the first place or because the archaeologist did not appreciate the chemical distinction between certain materials similar in appearance and put to similar uses.

The problem of making a correct identification of ancient materials from excavations may be very different from that of identifying the same materials in a fresh condition. It is usually less important to determine what it is now than to establish what it was originally before it underwent extensive chemical change. Though the original nature of inorganic materials may usually be determined with little difficulty, it is otherwise with organic materials, for these are likely to undergo complicated chemical changes during long burial in the ground.

Simple qualitative chemical tests are often sufficient to establish the identity of a material, but sometimes rather extensive tests are necessary, including complete quantitative analyses and measurements of physical properties. Micro-analytical methods are especially useful because it often happens that only small amounts of materials are available for investigation. For the examination of rare or valuable objects, which cannot be altered in any way even to the extent of taking samples for microanalysis, nondestructive physical methods must be used.

The exact identification of a large number of specimens of materials, and especially a chronological series of specimens, from a particular site or group of sites may yield valuable information about the cultural status or development of a people. The absence of metal among the remains of a given people obviously indicates a low state of technical development and a low state of general culture. The greater the variety of metals

and alloys utilized by a people, the greater their technical development, and, as a rule, the higher their general cultural development. The same appears to be true of certain kinds of nonmetallic materials such as glazes and glasses.

Some materials which serve as an index of cultural development may, of course, be recognized without chemical aid, but the application of chemical methods may make their recognition more certain. On the other hand, some kinds of materials which are indicative of cultural level are not easily recognized for what they are without chemical aid. For example, the introduction of lead into glazes, or the introduction of less common elements, such as cobalt, into glasses, represents technical advances which may be, and in fact sometimes have been, overlooked in the study of ancient remains.

Chemical methods are apparently not generally applicable to the important problem of determining the chronological sequence or absolute age of materials and objects, though they are applicable to a few kinds of materials and objects, especially when supplemented by other methods of relative or absolute dating. Ancient remains such as wood, textiles, and bones that contain carbon derived from plants or animals may now be dated absolutely by a measurement of the radioactivity of the carbon they contain, a method developed by W. F. Libby and co-workers at the University of Chicago. Its basic principle is that the carbon in the carbon dioxide of the atmosphere taken in by plants, both now and in ancient times, contains a fixed proportion of C^{14} with a half-life of about 5580 years.

During long burial in the ground a great variety of reactions occur between the material of most objects and the surrounding soil and ground water. (An example of this is the petrification of wood, wherein the organic components of the wood are gradually replaced by soil silicates.) The appearance and general condition of objects of the same material and of the same age taken from various excavation sites may be very different. A bronze from one site may be coated with a hard coherent layer of corrosion products of the type commonly called a patina, whereas a similar bronze of the same age from another site may be coated with a loose porous mass of corrosion products. Archaeologists observed that bronze found at Corinth was almost always in a severely corroded state, whereas similar bronze of equal or greater age found at certain other sites in Greece was not so corroded. It was found that the ground water at Corinth contains a high enough concentration of chloride to account for the severe corrosion of the buried bronze.

The deterioration of buried objects is predominantly the result of chemical change, and it is therefore reasonable to expect that the restoration of such objects should usually be best effected by chemical treatment. The deterioration of bronze, for example, is primarily the result of oxidation, and the reverse process of reduction should tend to restore corroded bronze to its original condition. This principle has been applied with much success

to the restoration of metal objects by various electrolytic reduction procedures.

The possibilities in the application of chemistry to archaeology have by no means been fully explored, and much of the work up to the present has been of a fragmentary and unsystematic nature. Enough has been done, however, to indicate clearly that this middle ground between chemistry and archaeology is capable of being developed into a distinct and systematic branch of applied chemistry with its own special data, techniques, and general rules.

EARLE R. CALEY

Cross-references: *Chemical Dating, Microchemistry*

ARMOUR RESEARCH FOUNDATION

Founded in 1936 to enable a group of staff members of Armour Institute of Technology, now Illinois Institute of Technology, to conduct industrial research on a contract basis, this Chicago organization headquartered at 35th and State Streets has become one of the largest research foundations in the world, with more than 1100 full time staff members working in 15 buildings and handling an annual volume of research expenditures of over \$11,000,000.

The Foundation conducts confidential research for industrial and governmental sponsors in the form of projects varying in size and duration depending upon their nature. Its research operations are organized into nine departments under chairmen. The departments in turn are divided into about 60 sections, each headed by a supervisor responsible for the technical conduct of the projects assigned to it. The names of the departments indicate the broad scope of the Foundation's activities: Ceramics and minerals; chemistry and chemical engineering; electrical engineering; heat power; international; mechanism and dynamics; metals; physics; and propulsion and structures.

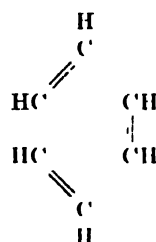
The several sections represent specialized fields of talent and experience. For example, the chemistry and chemical engineering department consists of eight sections: chemical engineering, physical chemistry, fine particles, biochemistry, organic chemistry, plastics, literature, and analytical. In addition to these, this department maintains three public service activities: (1) the National Registry of Rare Chemicals supplies valuable assistance in locating sources of supply of rare chemicals for users in all parts of the world; (2) the National Registry of Crystallographic Data furnishes summaries of crystal data for specific compounds to crystallographers throughout the world; (3) the department has been measuring and analyzing dustfall for the city of Chicago since 1946.

The chemistry and chemical engineering department is recognized for its "expert" status in the fields of fine particle technology, crystallography, lubricant technology, ozone technology, propellants, and rheology

CLIFFORD A. HAMPEL

AROMATIC COMPOUNDS

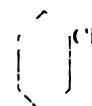
Compounds that contain a ring structure composed of one sort of atoms only are called homocyclic. These are divided into two groups (1) a relatively small number retain the essential characteristics of aliphatic compounds and are called *alicyclic compounds*; (2) most of the other ring compounds are related to benzene (C_6H_6) or its derivatives, and are called *aromatic compounds*. The name is associated with the penetrating odor of the first few compounds of this group that happened to be investigated, this odor was described as aromatic. The classification, however, is not limited to an odor or type of odor. Today all derivatives of benzene generally are classed as aromatic compounds, whether they have an odor or not. The benzene ring



is usually abbreviated by a simple hexagon. Thus



stands for C_6H_6 and

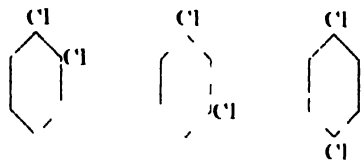


stands for $C_6H_5C^1$

Benzene has been studied by electron diffraction and x ray diffraction techniques. Evidence points to a ring of six carbon atoms that lie in one plane. One hydrogen atom is attached to each carbon atom. The spacing between adjacent carbon atoms in the benzene ring (1.39\AA) is less than that for a single bond space (1.54\AA), and close to that for a double bond space (1.34\AA). Benzene does not react, however, as if it had typical double bonds, nor does it show the typical reactions of an alternate double and single bond conjugated system. The chemical reactivity of benzene, however, is far greater than that of *n*-hexane (C_6H_{12}). Theorists have concluded that the correct structure of benzene probably resonates between all possible structures. The two forms that probably contribute most to the structure of benzene are

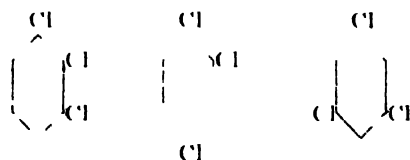


If one carbon atom in benzene is labeled 1, then the others are called 2 through 6 successively clockwise around the ring. If the ring has one hydrogen only substituted by halogen, for example, then only one such compound is known. One and only one chlorobenzene is known. This fact is taken as evidence that all the hydrogen atoms in benzene are equivalent. Three dichlorobenzenes ($C_6H_4Cl_2$) are known. These correspond to positions of the chlorine atoms 1,2 (ortho), 1,3 (meta), and 1,4 (para).



1,2 Dichloro 1,3 Dichloro 1,4 Dichloro
benzene, ortho benzene, meta benzene, para
Dichloro Dichloro Dichloro
benzene benzene benzene

In the case of three substituents the naming is as follows:



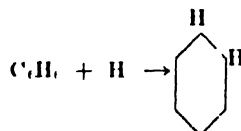
1,2,3 Tri 1,2,4 Tri 1,3,5 Tri
chloroben chloroben chloroben
zene, ortho zene, ortho zene, ortho
ortho Tri meta Tri
chloroben Trichloro Trichloro
zene benzene benzene

Benzene (C_6H_6) is a colorless liquid that boils at 80°C. It has an aromatic odor and it is immiscible with water. Like all hydrocarbons, it burns readily in air. Benzene, like acetylene, burns with a sooty flame, a characteristic attributed to the high percentage of carbon in the compound.

Benzene is obtained in great supply from the destructive distillation of coal, being fractionated from coal tar. It can also be made synthetically from petroleum or acetylene.

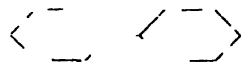
Benzene reacts with halogens to form products of varying halogen content: $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$. In a similar manner, substitution in the benzene ring can be accomplished by fuming nitric acid (in the presence of a strong dehydrating agent): $C_6H_6 + HONO_2 \rightarrow C_6H_5NO_2 + H_2O$, and by concentrated sulfuric acid: $C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$. Halogens can also add to benzene as well as substitute in the ring: $C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$. Cyclohexadiene, a compound that shows the reactions typical of a conjugated system, forms when benzene adds hy-

drogen in the presence of nickel as a catalyst:



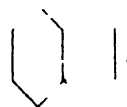
Benzene is a useful solvent and it is an additive in motor fuel because of its high antiknock value. It is the starting material from which a number of useful substances is made including styrene, chlorobenzene, phenol, nitrobenzene, diphenyl (biphenyl), phthalic anhydride, and others. The vapors of benzene are toxic.

Many compounds are known in which the benzene ring is attached to other benzene rings. This attachment can occur end to end as in diphenyl (biphenyl):

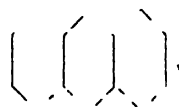


Diphenyl is formed when benzene vapor is partially decomposed by heating it above 600°C in the presence of iron. This colorless crystalline compound melts at about 69°C and boils at 254°C. It is stable enough to be used successfully as a heat transfer agent.

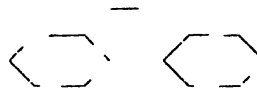
Side to side attachment of two benzene rings results in *naphthalene*:



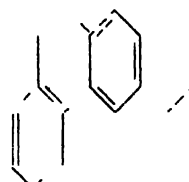
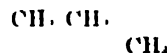
A compound obtained by the fractionation of coal tar and anthracene:



also from the same source. Derivatives of both compounds are used in dyes. Three benzene rings make *phenanthrene*:

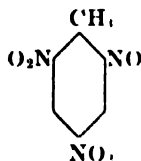


One of the compounds that contain multiple benzene rings are known to be carcinogenic (cancer-producing). Methylcholanthrene:



is one prominent example

The substituent CH_3 in the benzene ring forms *toluene*, $\text{C}_6\text{H}_5\text{CH}_3$, a well known hydrocarbon. Although some toluene is made from coal tar, most of it is manufactured from petroleum. Toluene is a colorless aromatic liquid that boils at 110.8°C . When strongly nitrated, it forms the well-known TNT, (symmetrical trinitrotoluene) that is a powerful explosive that can be handled with relative safety.



The next hydrocarbon in the series, is *ethylbenzene* ($\text{C}_6\text{H}_5\text{C}_2\text{H}_5$).

Three dimethylbenzenes or xylenes are known [*o*-, *m*-, *p*- $\text{C}_6\text{H}_4(\text{CH}_3)_2$]. They differ slightly in boiling points, and are used as solvents, often mixed in commercial preparations.

Styrene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$) is a liquid that boils at 146°C . It is an example of an unsaturated aromatic hydrocarbon. Styrene is the base material for the manufacture of many thermoplastic polymers (polystyrene).

All the classes of compounds known in aliphatic chemistry have their counterpart in aromatic chemistry. We shall limit our examples to a few illustrations of each sort.

Aromatic hydroxides are called *phenols*. Ordinary phenol ($\text{C}_6\text{H}_5\text{OH}$), which has been described as a pink slush, melts at 41°C and boils at 182°C . The compound has a characteristic penetrating odor. It is widely used in the manufacture of resins. Some phenol is obtained from coal tar, but most of it is manufactured synthetically.

1,2-Dihydroxybenzene (*ortho*) is called *catechol*, the *meta* compound (1,3-dihydroxybenzene) *resorcinol*, and the *para* compound (1,4-dihydroxybenzene) *hydroquinone*. Catechol is used in the synthesis of adrenaline, a powerful stimulant. Resorcinol is used to make hexylresorcinol, a urinary antiseptic. Hydroquinone is used extensively as a developing agent in photography. Trihydroxybenzenes are also known.

Phenols are not similar to alcohols in properties. An example of an aromatic alcohol is *benzyl alcohol* ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$). This compound and its esters are used in perfumes.

Diphenyl ether ($\text{C}_6\text{H}_5)_2\text{O}$ is a colorless solid that melts at 28°C . It has a geranium-like odor, and it is used as a heat-transfer agent because of its stability.

Aromatic aldehydes are represented by *benzaldehyde* ($\text{C}_6\text{H}_5\text{CHO}$) which is found in nature and is called oil of bitter almonds. Another important aldehyde is *vanillin* [4-hydroxy-3-methoxybenzaldehyde, 1,3,4- $\text{C}_6\text{H}_3(\text{CHO})(\text{OCH}_3)_2$], which is found in nature and which is manufactured synthetically.

Like aliphatic ketones, aromatic ketones may be simple or mixed. The least complicated of the simple ketones is diphenyl ketone ($\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$),

or *benzophenone*. Its melting point depends on the form it takes. It boils at 305°C .

The simplest aromatic amine is *aniline* ($\text{C}_6\text{H}_5\cdot\text{NH}_2$). Many derivatives of aniline are known. Aniline can be made by the reduction of nitrobenzene, or by the reaction of chlorobenzene with ammonia. Aniline is the parent compound of many dyes. Aniline tends to destroy red blood cells in the body, so it should be handled with care.

Aromatic acids of the carboxylic type are represented by *benzoic acid* ($\text{C}_6\text{H}_5\text{COOH}$) as the simplest member. Benzoic acid or its sodium salt is used extensively as a food preservative. Three phthalic acids (dicarboxylic) are known: phthalic anhydride [$\text{C}_6\text{H}_4(\text{CO})_2\text{O}$] is made from the *ortho*-form; it is important in the manufacture of resins, together with glycerol. Other important aromatic carboxylic acids include *cinnamic acid* ($\text{C}_6\text{H}_5\cdot\text{CH}=\text{CHCOOH}$), an unsaturated acid which occurs in nature, and *salicylic acid* ($\text{C}_6\text{H}_4\text{OHCOOH}$) which is both a phenol and an acid. Salicylic acid derivatives are widely used. Methyl salicylate is oil of wintergreen, and acetylsalicylic acid is aspirin.

The great variety of aromatic compounds is more fully appreciated when one realizes that substitution in the benzene ring by halogen, NO_2 , SO_3H , NH_2 , and other groups is possible. In addition, a great variety of side chains can be used, and also combinations of them. Many of the aromatic compounds are extremely valuable as medicines, dyes, antiseptics, anesthetics, and flavorings.

ELBERT C. WEAVER

Cross-references: *Aliphatic Compounds*, *Allylic Compounds*

ARRHENIUS, SVANTE AUGUST (1859-1927)

Born at the estate of Wik, near Lake Malar, Sweden. In 1884, his classic doctoral thesis, "Recherches sur la conductibilité galvanique des électrolytes" was reluctantly accepted by the University of Upsala. This work expounded for the first time the theory of electrolytic dissociation. Arrhenius visited Ostwald in Riga, Kohlrausch in Würzburg, Boltzmann in Graz, and van't Hoff in Amsterdam. In 1887 he published a much matured version of his theory in the *Zeitschrift für Physikalische Chemie*. The essential qualitative idea of his theory, which is now a cornerstone of physical chemistry, is that acids, bases and salts split up spontaneously in water and some other solvents. With this idea, and a quantitative method, since greatly modified, of calculating the degree of electrolytic dissociation, Arrhenius was able to explain an extraordinarily wide number of phenomena, e.g., the constancy of the heat of neutralization, the high osmotic pressure of electrolytes, the increasing molar conductivity and osmotic pressure of electrolytes with dilution, the equal chemical activity of all strong acids, etc. Another fundamental contribution to chemistry was his suggestion that only "activated" molecules, bearing energies higher than

average, can undergo chemical reaction. It remains the basis of our views of the mechanism of chemical reactions. In particular, the Arrhenius equation for the variation of the rate of a chemical reaction with temperature (1889) is very widely applied. Arrhenius received the Nobel prize for chemistry (1903), the Davy Medal of the Royal Society, and the Faraday Medal of the Chemical Society.

BERNARD JAFFE

ARSENIC AND COMPOUNDS

Arsenic, symbol As, is a brittle, steel-gray metal of atomic number 33 and atomic weight 74.91. It is located in Group V A of the Periodic Table with nitrogen, phosphorus, antimony and bismuth, and is 47th in order of occurrence of the elements in the earth's crust. Its compounds, such as the oxide, As_2O_3 , and the sulfides, have been known since ancient times. While native arsenic has been found, it most commonly occurs as the arsenides and sulfarsenides of heavy metals like copper, lead, gold, cobalt and iron. As a frequent constituent in many ores it is derived chiefly as a by-product in the production of metals, almost always as arsenic trioxide, or "white arsenic," As_2O_3 . When arsenic containing ores are roasted in the air, As_2O_3 sublimes, is condensed as a dust, and then recovered as a high purity material. Arsenic can be sublimed from arsenopyrite minerals, e.g., $FeAsS$, and purified by repeated sublimations in the presence of carbon. It can also be obtained by the reduction of As_2O_3 with carbon. The available supply of arsenic trioxide has exceeded the consumption for many years. The current price of arsenic metal is 60¢ per pound, and that of arsenic trioxide is 5.5¢ per pound.

The physical properties of arsenic include: density, 5.73 g/cc (crystalline form); melting point, 811°C (36 atmospheres); boiling point, sublimes 610°C; specific heat, 0.082 cal/g/°C (0°-100°C); latent heat of fusion, 88.1 cal/g; latent heat of vaporization, 411 cal/g; coefficient of thermal expansion, 1.7×10^{-5} (25°C); electrical resistivity, 33.3 microhm-cm; hardness, 117 Brinell; thermal neutron absorption cross section, 4.3 barns. Arsenic crystallizes in the rhombohedral system, and two other forms exist; black amorphous (density, 3.7) and yellow cubic (density, 2.0).

Arsenic tarnishes in air and when heated in air or oxygen burns to form As_2O_3 . It is oxidized to orthoarsenic acid, H_3AsO_4 , by concentrated HNO_3 or H_2SO_4 , and is slowly converted to $AsCl_3$ by concentrated HCl in the presence of air. The halogens react with it directly to yield the trihalides; the only pentahalide known is AsF_5 . When fused with alkalis like $NaOH$, arsenic forms arsenites, AsO_2^- . It unites directly with many metals to give arsenides of definite composition, e.g., Zn_3As_2 , Mg_3As_2 , $CoAs_2$, etc., and reacts with sulfur to form di-, tri- and pentasulfides: As_2S_2 (realgar), As_2S_3 (orpiment) and As_2S_5 . Trivalent and pentavalent arsenic oxides, oxygen

acids and salts and thio salts are known. Arsenic trioxide is the most important compound of arsenic. It is oxidized by HNO_3 or Cl_2 to orthoarsenic acid, from which arsenate salts are made by neutralization. Arsine, AsH_3 , is formed when arsenic compounds are placed in a zinc- H_2SO_4 hydrogen generator, as in the Marsh test for detecting traces of arsenic. It is an extremely poisonous gas that dissociates into H_2 and As when heated.

Arsenic has no use as a pure metal, but when alloyed in small amounts with lead increases the hardness of lead-base bearing materials and forms more perfect spheres when making lead shot. Small amounts increase the corrosion resistance and toughness of copper. These alloying uses consume only a few hundred tons per year.

Long regarded as synonymous with the word "poison," the toxic nature of arsenic in compounds accounts for its major applications as insecticides (Paris green, or copper acetoarsenite, lead and calcium arsenates, etc.), wood preservatives (sodium arsenate, As_2O_3 , etc.), pharmaceuticals (Salvarsan, Neosalvarsan, etc.), sheep dip, poisoned baits, weed killers (sodium arsenate), and hide preservatives. All these products are derived from As_2O_3 , which is also used directly in glass manufacture. Adamsite and lewisite are important arsenic-containing chemical warfare agents. The greatly expanded usage of organic insecticides has made profound inroads into the consumption of arsenical insecticides, the principal outlet for arsenic. For example, the consumption of white arsenic, As_2O_3 , in 1952 was 16,000 tons, a 14% decline below 1951. A serious problem faces the nonferrous metals industry which perforce must find new outlets for by-product As_2O_3 or dispose of it in a safe manner.

The most effective antidote for arsenic poisoning is freshly prepared ferric hydroxide (from ferric chloride and milk of magnesia) which forms an insoluble nontoxic compound with arsenic trioxide.

CLIFFORD A. HAMPLI

ASBESTOS

Asbestos is a broad term applied to a number of fibrous mineral silicates found in the natural state in the earth: actinolite, anthophyllite, amosite, chrysotile, ercoidolite, and tremolite. The most important single source of chrysotile asbestos is the province of Quebec.

The structures of asbestos fibers have been studied by many investigators using x-ray diffraction patterns as a method of identification and classification. These patterns have been fairly well established for the amphibole group; those of the serpentine group, which includes chrysotile asbestos, have been the subject of recent intensive studies that have indicated that the fibrils are tubular. The curled structure of chrysotile has been discussed in detail by applying the theory of diffraction and small angle dispersion, wide-angle interferences and displacement growth of volutes.

Most asbestos fibers appear in nature as parallel



Fig. 1. Electron micrograph of asbestos fibers (about 25,000X).

fibrils closely packed and at right angles or parallel to the wall rock. In some cases, the amphibole fibers have random orientation and appear as mass fibers with weak bonding structure. Fiber lengths vary from microscopic to one inch and longer; cross-sections of fiber bundles, from 10 microns and larger to submicroscopic measurements of 300Å or less. Asbestos fibers contain individual fibrils smaller than any other known natural fiber, and this may be one reason for their great reinforcing strength.

The approximate chemical analyses of five asbestos fibers are as follows:

(Expressed in percentages)			
	Amosite	Anthophyllite	Chrysotile
SiO ₂	49-53	56-58	37-44
MgO	1-7	28-34	39-41
FeO	34-44	3-12	0.0-6.0
Fe ₂ O ₃	—	—	0.1-5.0
Al ₂ O ₃	2-9	0.5-1.5	0.2-1.5
H ₂ O	2-5	1.0-6.0	12.0-15.0
CaO	—	—	Tr-5.0
Na ₂ O	—	—	—
	Crocidolite	Tremolite	
SiO ₂	49-53	51-62	
MgO	0-3	0-30	
FeO	13-20	1.5-5.0	
Fe ₂ O ₃	17-20	—	
Al ₂ O ₃	—	1.0-4.0	
H ₂ O	2.5-4.5	0-5.0	
CaO	—	0-18	
Na ₂ O	4-8.5	0-9	

The effect of temperature on the loss in weight

of chrysotile asbestos is shown below. Its water of crystallization at temperatures above 1000°F is driven off, leaving the fiber in a weakened condition, which eventually changes the x-ray diffraction pattern of chrysotile to that of forsterite, then olivine at temperatures of 1500°F and higher. The amphibole fibers are more resistant to heat and remain in fairly good condition until high temperatures cause oxidation of the iron, or fusion sets in.

EFFECT OF TEMPERATURE ON LOSS IN WEIGHT OF CHRYSOTILE ASBESTOS FIBERS

Temp. °F	Time	% Loss in Weight Chrysotile
400	2 hr.	0.30
600	2 hr.	0.85
700	2 hr.	1.78
800	2 hr.	2.17
900	2 hr.	2.83
1,000	2 hr.	3.99
1,100	2 hr.	10.38
1,200	2 hr.	12.75
1,400	2 hr.	13.43
1,500	2 hr.	—
1,600	2 hr.	13.62
1,700	2 hr.	—
1,800	2 hr.	13.77

Asbestos fibers are extracted from the ore in a manner different from normal ore-dressing methods. The ore is first crushed to convenient handling size by a series of jaw crushers, cone crushers, or sometimes rolls. This crushed ore, which is about $\frac{5}{8}$ to 1 in. in cross section, is dried by conventional horizontal rotary driers or by vertical driers and conveyed to a storage building to allow additional "aging." The ore is then drawn off at the bottom of the storage bin and screened over large mesh screens to separate the large pieces of uncrushed ore from the fine ore and liberated fiber. At this stage, the large pieces of ore may be further opened by crushing or by some type of hammer mill.

Screening of the crushed ore and fiber is usually accomplished by some type of shaking screen with a small gyratory motion to aid the movement of the ore and fiber down the slope of the screen. Near the lower end of the screen is a suction hood at a point 3 or 4 in. above the moving material to pick up the loosened fiber which works to the top layer of rock and to aspirate it into a collector. In the first screening operation, the screen meshes are usually of the order of $\frac{1}{2}$ to $\frac{1}{4}$ in. and are decreased in size as the ore becomes smaller. The entire operation consists of numerous screenings, crushings, and aspiratings of the recoverable fibers until all fibers of any commercial value are recovered. The different fiber sizes removed from the various screens are later treated separately by mechanical willows that fluff the fiber to produce various grades directly or to regrade it to meet the specifications established by the Quebec Asbestos Mining Association. All extremely short fibers and dusts are picked up by collectors or bag filters and graded as shorts or floats for industrial use.

The most important uses of asbestos fibers are in asbestos-cement products, such as shingles, pipes, board, and corrugated and flat sheets. Asbestos is used also in papers, textiles, packings, floor tiles, cements, plastics, roof coatings, putties, insulating jackets, insulating blocks, friction materials, millboards, welding rods, paints, pipe coverings, and filter media. Approximately 1,600,000 tons of asbestos of all grades and varieties were used throughout the world during 1955.

M. S. BADOLLET

ASPHALT

Asphalt is man's earliest organic engineering material. Its use as an adhesive and waterproofing material dates back to the dawn of civilization. It is still used for these purposes today; huge quantities are employed in roadbuilding, roofing and various types of repair work where its waterproofing properties are required. It is also used in minor quantities in rubber and adhesive compounds, rope sizing, insulation, etc. The words *bitumen* and *asphalt* are often confused. To eliminate this confusion the ASTM established these definitions in 1935:

(A) Relating in general to bituminous materials. *Bitumens*: Mixtures of hydrocarbons of natural or pyrogenous origin, or combinations of both, frequently accompanied by their nonmetallic derivatives, which may be gaseous, liquid, semisolid, or solid, and which are completely soluble in carbon disulfide.

(B) Relating specifically to petroleum asphalts. *Asphalt*: A dark brown to black cementitious material, solid or semisolid in consistency, in which the predominating constituents are bitumens which occur in nature as such, or are obtained by refining petroleum.

The general connotation of *asphalt* implies also the crude mixture of bitumens with adventitious impurities, such as silt, clay, or mineral matter. Another term commonly used is *natural asphalt*, (asphalt containing impurities and found in nature, (Cuban, Trinidad, etc.). Occasionally the term *natural bitumens* is used those found in nature but free of mineral matter and also soluble in carbon disulfide (wurtzilite, gilsonite, impsonite, elaterite, and grahamite).

The world's largest deposits of asphalt, rivaling the Middle East oil fields, are the Athabasca tar sands of Canada. Recent estimates give the area as 30,000 square miles, estimating a reserve of this asphaltic oil, or liquid asphalt, as somewhere between 200-300 million barrels. It also occurs in California, Mexico, Trinidad, Venezuela, Iran and other oil-bearing regions.

Commercial Asphalts. There are five commercial types of asphalts in use today. They differ as to their origin, purity, and chemical constitution:

(A) *The natural asphalts* of high purity, often designated as "natural bitumens" (gilsonite), usually mined as solid material, used mostly in special lacquers in the insulation field.

(B) *The natural impure asphalts*, such as the Trinidad and Bermudez Lake, and small amounts

of native Cuban asphalt. Trinidad asphalt contains about 34% of fine (colloidal) clay or mineral matter.

(C) *Petroleum or oil asphalts.* The latter have also been designated as "artificial asphalts". This constitutes by far the largest quantity of asphalt used today. In the vacuum and steam distillation of asphaltic petroleum, crude oil is reduced to the penetration, or hardness, to fit various specifications. This produces the so called "straight-run", or paving, asphalts. Soft or fluid residues are also produced by this method and are termed "fluxes".

(D) *Roofing or "blown" asphalts.* Following the above straight-run, vacuum asphalts in value and in quantities consumed are the blown types made by oxidation of a straight-run petroleum residue or flux. Oxidation is carried out by the use of air at from 450-600°F, obtaining roofing and specialty asphalts, usually of rubber or gel character.

(E) *Cracked asphalts* are a by-product in oil-cracking operations. The fluid residuum, or cracking coil tar, as by product is used in the form of road oils or is steam-reduced to hard consistency. These materials are characterized by high susceptibility to temperature changes.

Physical Constitution. Asphalts free from inorganic matter and the hydrocarbons composing them are almost completely soluble in carbon disulfide, carbon tetrachloride, pyridine, and similar solvents. A small percentage (less than 0.5% of the total soluble material) may be insoluble in benzol or carbon tetrachloride due to traces of cracked material called carbenes or carboids. The portion insoluble in carbon tetrachloride but soluble in carbon disulfide is termed "carbene", a word coined by Richardson in 1905. He believed these were deleterious products formed by cracking or overheating. MacKenzie studied these materials in 1920 and greatly contributed to a knowledge of test methods.

Asphalts are only partially soluble in low-boiling paraffinic hydrocarbons, such as 86 B \acute{e} . paraffinic naphtha, pentane, propane and hexane; these hydrocarbons dissolve the oil and resins, precipitating the asphaltenes.

In studying the various so called "groups" in asphalts, it is customary to work with the pure material, free of mineral or inorganic material; the petroleum asphalts, already free of ash, are separated directly. In the case of the natural asphalts containing mineral matter, etc., these impurities must be first removed by solution and filtration.

Designation of soluble constituents. The distinctive character of the naphtha insoluble material gave rise to the concept that ash-free asphalts are physically not homogeneous materials, but appear to be of quite heterogeneous character, depending on the temperature. This led early investigators to employ various solvents for identification and classification purposes.

Methods of group separation. Procedures used today are based on the earlier work of Marcusson:

(A) *Asphaltenes*: the insoluble matter or precipitate formed when asphalts are treated with a 5-10 volume excess of pentane, hexane, or 86-88 B \acute{e} . paraffinic naphtha usually in the boiling range

of 40–60°C. Empirical formula probably $C_{18}H_{16}S_2$; m.w. 1216 (Bestougeff).

(B) *Petrolenes* (malthenes, maltenes): the portion soluble in the above solvents. Marcusson further split (B) into resins and oils by adsorbing fraction (B) on Fullers' earth, alumina, and other adsorbents, obtaining the unadsorbed oils, and extracting the adsorbent with chloroform to obtain the resins. Investigators today also use advanced chromatographic techniques.

ASPHALTIC BITUMEN		ASPHALTENES	CARBONS	MINERAL MATTER
SOLUBLES IN CARBON DISULPHIDE				
SOLUBLES IN CARBON TETRACHLORIDE				
SOLUBLES IN PETROLEUM ETHER				
NOT AFFECTED BY ADSORBENTS	REMOVED BY ADSORBENTS			
OILY CONSTITUENTS	ASPHALTIC RESINS			
MALIENES				

Fractional Constitution of Asphaltic Bitumen as Determined by Selective Solvent Analysis. (Neppe)

Chemical Constitution

Asphaltenes. This group is precipitated by low-boiling, paraffinic hydrocarbons. They are normally brown to black, hard, friable, infusible powders, insoluble in acetone, ethyl ether, dilute alcohol, but are soluble in polar solvents, such as pyridine, nitrobenzene, carbon disulfide, carbon tetrachloride, benzene, etc.

Asphaltenes react with sulfuric acid, forming sulfonation products, soluble in water. They also react with nitric acid, and can be condensed with formaldehyde to give the so-called formolites of Nastjukoff. This reaction is not undergone by the paraffins, olefines, naphthenes, ketones and sulfur compounds, but primarily by cyclic unsaturated compounds also found in the resin group. The asphaltenes may be hydrogenated to form resins.

The range of values is broadly between 900–140,000 by the monomolecular film method and of a lower range from 1200 to 1400 for very narrow and precisely separated fractions. (Bestougeff).

The carbon-hydrogen ratios are generally close 10:1, the range being from 9.3–12.1. Cracking still residual asphalts show more clearly a ratio of 12:1. The hydrogen content is lower than in the case of the resins. Sulfur is concentrated in this fraction and may be as high as 8–9% for asphalts showing a total sulfur of 6–6.5%.

Resins. This group comprises semisolid to solid, dark-colored materials showing extremely high ductility and great adhesivity. They are soluble in the petroleum low-boiling hydrocarbons which precipitated the asphaltenes and are also soluble in polar solvents, benzene, chloroform, but not entirely in propane and lower molecular weight hydrocarbons, or gaseous petroleum fractions. These materials are easily hydrogenated to oily materials and are converted to asphaltene material by oxidation. They may also be sulfonated, forming ill-defined sulfonates and sulfonium compounds.

The molecular weights of the resins lie in the

range of 800–900. Bestougeff shows values of from 900–1300 by viscometric methods.

The carbon-hydrogen ratio is approximately 8:1. Bestougeff obtains a ratio of 9.6:1 for narrow chromatographically separated cuts, and 10.1 for a California resin.

The resins generally show more hydrogen than the asphaltenes but also less sulfur. By drastic hydrogenation they may be converted to oily materials of lower molecular weight.

The resins are quite free of saturated hydrocarbons. Those compounds which are rich in nitrogen are derived from high nitrogen-content California type crudes. The molecular weight and C/H ratios of the resins overlap the constants given for the asphaltenes.

Oils. The oily components which are the dispersion media (external phase) for the peptized asphaltenes or micelles, are exceedingly high-boiling hydrocarbons, similar to the lubricating oils in crude petroleum. These oils may be paraffinic and contain solid waxes in addition; they may also be of so-called naphthenic, or naphthenoaromatic nature, of low viscosity index, with or without solid waxes. The oily groups are soluble in low boiling petroleum ether and most other organic solvents. The oils, as the resins described above, are also soluble in pentane, hexane.

Physically they appear as yellow to reddish colored oils of semisolid consistency, showing a bluish or greenish cast by reflected light. They are usually of saturated nature although the iodine number may be relatively high, depending on the origin (derived from vacuum asphalts or cracked products).

They may be converted to resins in dehydrogenation reactions; the generally saturated portions of the oil group are, in the main, stable to air or oxidation reactions; condensation reactions such as the formolite reaction, often take place with some portion of the oils (cyclics). Gruse and others consider asphalts to be derived from crude petroleum by oxidation, dehydrogenation, and sulfurization reactions forming first the resins, carboxylic acids, etc.

The molecular weights of the oils are in the range of about 280 to slightly over 600, the average about 450; Hoiberg states that molecular weight values range from 290 to 630, for six asphalts investigated.

The carbon-hydrogen ratio for the oily components ranges from 6.8 to slightly over 8.0; a useful constant to determine the types of hydrocarbons present in oily fractions is known as the U. O. P. characterization factor. This constant will range from about 10.4 for the oils from highly cracked asphalts to 12.05 for oils from the Mid-Continent paraffinic types. A general average formula for the oils lies in the area of from $C_{18}H_{24}$ to $C_{24}H_{32}$.

Cracked Asphalts. Asphalts derived from oil-cracking processes are very adhesive but highly temperature-susceptible. Usually free of carboids, they may show carbene material.

Blown Asphalts. Discoveries of new oil-producing areas after the early discoveries in

Pennsylvania led to the development of Ohio and Indiana crude oil. These semiasphaltic and part-paraffinic crudes produced waxy residues quite unsuitable for roads or roofing purposes.

Blown asphalts suitable for roofing purposes are processed so as to produce a "rubbery" or tough structure in the bitumen. These asphalts show properties quite different from the straight-run, or vacuum, asphalts.

	Vacuum Asphalt	Air-Blown Asphalt
Penetration index (Pfeiffer-Van Door-mal)	Approx. 0 to -1.0	Over 1.0
Fluidity at temperatures over 200°F	High	Low
Ductility at 77°F (cm)	High	Very low

By air-blowing, products of high melting point are formed. The latter increases with time of blowing. The increase in asphaltene at the expense of resins and oils is very pronounced in blown asphalts.

The reactions taking place in this process (200–325°C) are primarily those of dehydrogenation, water being a by-product in all blowing operations. $R-HR' + O \rightarrow RR' + H_2O$. During this phase, or early stage, the iodine number remains constant; with long duration of blowing the reaction is probably: $>CH-CH< + O \rightarrow >C=C< + H_2O$.

In order to simplify the study of asphalts recent investigators prefer to regard the mixture of resins and oils as the total dispersion medium for the micelle. This mixture of oils and resins is commonly called the petroleum or maltheine fraction.

Structure of Hydrocarbon Groups. Structure varies considerably, depending on the origin of the asphalt. The carbon skeleton is most important. It forms the greater portion of the molecule and is highly cyclic. As the rings result from copolymerization of simpler elements, the asphaltene molecule may be considered as ring type.

The oil components in asphalts are structurally very similar to the lubricating oils from petroleum. They are composed of single or condensed naphthene rings containing several side chains of varying lengths. The greater the number of these aliphatic side chains, the nearer the total molecule approaches true paraffinity; the longer the side chains the higher is the solidification point of the hydrocarbon. Beside the naphthene type rings present also are the alkylated aromatic hydrocarbons of very high boiling point. Rossini and collaborators have verified the presence of the latter types in a so-called paraffin-base crude from the Ponca City oil field. The total oily hydrocarbons may also be a composite group with rings or nuclei of from 3 to 6 in the molecule, of which one to four may be aromatic.

The paraffinic or the aromatic or naphthenic nature of the oils greatly determines the extent or degree of the heterogeneity of asphalts, and their behavior in use; this homogeneity is closely related to the fineness of the asphaltene dispersion, dependent on the low or high degree of paraffinity or aromaticity of the oils. Assuming the

same content and type of resins, the asphaltene micelle is best peptized in oils of aromatic or naphthenic nature, resulting in homogeneous asphalts, or those in which the asphaltene are almost in true solution.

Neighboring nuclei could easily condense or cyclize at points a, b, c, etc.; the structure must be visualized as three-dimensional.

Any porphyrin compounds of vanadium and the heavy metals will be present in the asphaltene fraction so that great care is necessary in the separation and analytical techniques.

The resins also appear to be devoid of aliphatics. Their structure is in the main naphtheno-aromatic, with atoms of sulfur or oxygen in bridge linkage. As to the latter elements including nitrogen, it has been found that the sulfur linkages appear in the groups derived from decidedly high sulfur asphalts (Mexican and the Mid-East asphalts), the oxygen groups or linkages in Baku and the Texas type resins, with fairly high nitrogen content linkages in those resins from the heavy base asphalts of California origin.

As stated above, the structure of the resins is, in general, similar to that of the asphaltene, with perhaps much longer alkyls or more numerous chains in the molecule. There is considerable overlapping in the molecular weight and C/H ratio of the resins and asphaltene.

E. J. BARTH

Rheology. For many applications the flow or rheological properties of asphalt are of primary importance. Asphalts can be divided into two general classes: those with purely viscous flow characteristics and those with plastic characteristics.

When the various components which constitute an asphalt are in a state of true solution, the asphalt has the characteristics of a purely viscous liquid. The application of a stress to such a material will produce a deformation which is directly proportional to the applied stress and the viscosity of the material will be independent of the shearing rate. Most of the asphalts used in road construction and manufactured by vacuum flashing or vacuum distillation of petroleum closely approach this type of rheological behavior.

When the solubilizing power of the lower molecular weight components of the system is not sufficient to maintain the less soluble components (polar compounds, higher molecular weight aromatic compounds and higher molecular weight organic sulfur, nitrogen and oxygen compounds) in solution, the occurrence of molecular association between various of these components leads to the formation of sufficient intermolecular structural characteristics to confer on the system the rheological properties of colloidal systems. These properties include elasticity, the existence of a yield value and variation of viscosity with shearing rate. When such a material is subjected to a small stress, an elastic deformation occurs, and on removal of the stress the material rebounds to its original position. If the applied stress is increased sufficiently, there will occur a permanent deformation beyond the elastic deformation which is not recovered when the stress is removed. The point

at which this phenomenon is first observed is termed the yield value or yield stress. This characteristic is of great practical importance in roofing applications and in other instances where the asphalt is placed on a sloping surface where it is subjected to a continual small gravitational stress. Even the hardest asphalt will gradually flow under such stresses unless its yield value exceeds that of the applied stress. When the viscosity of such materials is determined, it is found that the observed value of viscosity decreases as the rate of shear is increased. This characteristic is of value in applications which require the asphalt to survive sudden applications of stress which produce high rates of shear.

The imperfect solubilization of the higher molecular weight and more polar components engendering these plastic properties may be brought about by an insufficient concentration of lower molecular weight aromatic and heteroaromatic components as a result of (1) natural occurrence of a high ratio of paraffins and naphthenes to aromatics and heteroaromatics, (2) conversion of low and medium molecular weight components into high molecular weight components of low solubility by means of coupling reactions such as those which occur in oxidation of asphalt at elevated temperatures, or (3) decreasing the relative concentration of solubilizing components by the addition of paraffinic and naphthenic components to the system. Most of the processing of asphalts is designed to accomplish changes in rheological characteristics by one or more of the latter two mechanisms. For a comprehensive discussion of the rheological properties of asphalts and their dependence on composition, see Pfeiffer, *et al*, "The Properties of Asphalt Bitumen."

Action of Acids at Ordinary Temperatures. Asphalt resists attack by dilute sulfuric acid and hydrochloric acid in all concentrations; it is attacked by concentrated sulfuric and by nitric acid in all concentrations. Concentrated sulfuric acid converts the aromatics and heteroaromatics into preferentially water soluble sulfonic acids. The combined oxidizing and nitrating power of nitric acid leads to products containing nitrogen, little is known of their composition, although nitroaromatics are believed present. Paraffins and naphthenes generally are not attacked by sulfuric acid. The passage of hydrogen chloride gas through the material results in appreciable hardening, the extent depending on the amount of nitrogen bases converted to hydrochlorides or polymers.

Action of Alkalies. Asphalt is not attacked by concentrated alkaline solutions at ordinary temperatures, but dilute alkaline solutions react with acidic constituents to form salts such as sodium naphthenates which serve as excellent emulsifying agents for the asphalt.

Action of Sulfur. Reactions between asphalt and sulfur take place at temperatures above about 350°F to give products of high molecular weight and low solubility. This is not exactly analogous to the vulcanization of rubber, since olefins usually are not found in asphalts. Rather, the reactions of sulfur with asphalt are similar to those of oxygen,

wherein most of the sulfur is released as hydrogen sulfide and only a small part remains. Dehydrogenation-coupling reactions probably are important as in the case of oxygen.

Action of Halogens. The reactivity of halogens and halogenated compounds with asphalt decreases in the order, chlorine, bromine, iodine. Chlorination at 200°F produces high molecular weight material of low solubility, which on further heating gives off hydrochloric acid. At higher temperatures, 400-500°F, little of this chlorine reacted remains in the asphalt but appears primarily as hydrochloric acid. The high temperature chlorination produces a material quite similar to that which results from air blowing at the same temperatures. Treatment of asphalts with boiling halogenated solvents generally results in some loss of halogen from the solvent and in hardening of the asphalt.

W. C. SIMPSON

ASSAY

Assay, as generally used today, implies an analysis for only a certain constituent or constituents of a mixture, the others generally being neglected. The term is more generally applied to ores, alloys, and pharmaceutical preparations. The analysis of the principal component as given in the specifications of some industrial chemicals is referred to as assay.

Chemical assay methods are divided into two classes, dry and wet. The assay of rock for gold is the best known of the dry or fire methods. The ore is finely ground and mixed with charcoal and an appropriate flux, the composition of which depends upon the acidic or basic nature of the ore. The mixture is slowly brought to red heat. The gold, lead and silver separate as the free metal as a button in the bottom of the crucible and is separated from the slag by breaking the mass with a hammer. The lead and silver are separated by various methods and the free gold is finally weighed. Among the oldest of the wet methods is the assay of certain plants for the alkaloid content. The dried plant material is extracted with a solvent and the active constituent separated from the extract by chemical means.

Pharmaceutical preparations generally contain one or more active ingredients mixed with inert fillers, binders, etc., or dissolved or suspended in a liquid. The finished product must be assayed to determine whether or not it contains the stated amount of the active constituent (g) per unit (capsule, ampule, tablet or unit of volume).

The newer field of assay, *biological assay*, generally referred to as *bioassay*, is a test of the reaction of living organisms to a substance. The organisms used include single and multi cellular plants and animals. Assay using single cell organisms is called *micro-biological assay*. The most familiar technique is the "plate assay" used for testing antibiotics against various strains of bacteria.

Not only is bioassay used to control the quality of many pharmaceutical preparations and animal

feed supplements, but it is an important research tool. The search for new antibiotics and vitamins depends on this method of analysis for detection and initial evaluation. The feed supplements for cattle, hogs and chickens that promote more rapid growth and immunity to certain costly diseases are developed by feeding tests with the animal concerned. The screening of chemicals as insecticides is made with insects. A household insecticide for flies and mosquitoes, for instance, is evaluated for its effectiveness by the percentage of "kill" of these insects under a given set of conditions.

JOHN A. RIDDICK,

ASSOCIATION

Association is distinguished from true chemical polymerization by the type of bond and the thermal properties. Polymerization is a chemical reaction involving the formation of an nonionizable covalent bond; association involves the formation of polymeric compounds by a hydrogen bond or a similar bond. The thermal properties of the bond types also differ. The heat of formation and dissociation are less for the hydrogen bond than for the covalent bond and other bond types. The energies of dissociation for the hydrogen bond are usually about 5, never more than about 10 kcal per mole. Other types of bond dissociations are in the 25-100 kcal per mole range. The bond lengths are greater for the hydrogen bond than for other types of bonds.

Hydrogen bonding and association takes place between like and unlike molecular species. Association of like species is demonstrable by one or more of the several molecular weight methods. Association between unlike species is demonstrable by deviation from Raoult's law. The association of one component of a binary system can also be demonstrated by deviation from Raoult's law.

The strength of the hydrogen bond increases in the order FHF , OHO , OHN , NHN , and CHO , but they are dependent upon the geometry of the combination and the nature of the near elements upon resonances and also on the acid and base characteristics of the groups. The factors affecting the strength of the hydrogen bond also influence the degree of association. Some molecules form only dimers, some trimers, and others associate to the full possible four hydrogen bonds per molecule.

Association is accompanied by an increase in heat of fusion and heat of vaporization. The latter results in a longer free evaporation time. Ether, which is lightly hydrogen bonded, has a low boiling point and a low heat of vaporization, whereas 1-butanol with the same molecular weight and elemental composition has a much higher boiling point and heat of vaporization.

When an associated substance is added to a non-associated one, it would be expected that the association of the associated molecule would decrease. However, aniline, an associated liquid, if mixed with hexane, a nonassociated liquid, shows an increase in association. This association is not

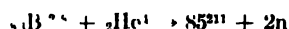
readily explained, but is probably a type of aggregation or association in which the internal pressure or attractive force between the molecules is so great as to resist dispersion.

JOHN A. RIDDICK

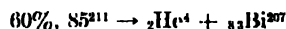
ASTATINE

The fifth member of the halogen family indicated by a vacancy in the early periodic tables was called ekaiodine. When atomic numbers were established, it became element 85 (Group VII of the Periodic Table). As early as 1926, lines observed in spectra corresponded to those predicted for element 85. During 1931-2, Allison secured data which were interpreted as evidence of the presence of element 85 in very low concentrations in aqueous extracts of monazite sand. He suggested that the element be named *alabamine* and its symbol be *Am*. In 1937, De reported that he had found element 85 in Travanore monazite and had prepared it in quantities large enough for visible observation. He suggested that it be named *dukin*. In 1940, Minder reported that RaA , an isotope of element 84, decomposed in very small part by radiating β -particles, and must therefore form element 85. He suggested the name *helvetium* and the symbol *Hlv*.

Early in 1940, Corson, MacKenzie and Segre reported that the bombardment of bismuth with 32 mev α -particles produced a substance or substances which furnish α -, β -, and γ -radiations. The α radiations were 60% of range 6.1 cm. and 40% range 4.2 cm. Tests seemed to show that the reactions were represented by the nuclear equations:

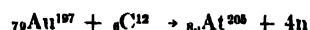


followed by two reactions:



These results were confirmed, and in 1947, when Corson, MacKenzie and Segre suggested that the element be named *astatine* (from a Greek word meaning "unstable") and its symbol be *At*, all other designations were discontinued. The International Union of Pure and Applied Chemistry has adopted this name and symbol.

Astatine is one of the elements in the principal chain of the radioactive series containing neptunium called the $(4n + 1)$ series. It is produced by bombarding nuclei near it in atomic number by particles accelerated in cyclotrons. When gold is bombarded by stripped carbon atoms one result is represented by the equation:



Isotopes of all atomic weights from 205 to 218 inclusive except 213 have been reported. Those with masses from 206 to 211 inclusive have half lives between 1.7 and 8.3 hrs; those of the other isotopes are fractions of a second.

Astatine prepared by bombarding bismuth with α -particles to form At^{211} has been the principal source of this element. The half life of this isotope 7.5 hrs. Using micro amounts and tracer techniques it has been found that astatine (1) behaves as a halogen, (2) is more metallic than iodine, (3) occurs in aqueous solutions as a univalent negative ion, (4) has at least two positive oxidation numbers, (5) can be deposited on the anode by a direct electric current, (6) can be vaporized from molten bismuth and condensed on a very cold receiver, (7) is precipitated as a sulfide, (8) injected in guinea pigs, accumulates in the thyroid, (9) is very destructive of thyroid tissue for a short range without involvement of the parathyroid, (10) the free element dissolves in organic solvents.

F. E. BROWN

ASYMMETRY

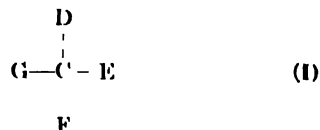
Asymmetry involves the presence of four different atoms or substituent groups bonded to an atom. Its existence was discovered in 1815 by the French physicist J. B. Biot (1774-1867). He found that oil of turpentine, and solutions of sugar, camphor, and tartaric acid all rotate the plane of plane-polarized light when placed between two Nicol prisms. This phenomenon is called optical rotation and is indicated in symbols in the following manner: $[\alpha]_D^{20} = +53.4$ aq, meaning that the substance gives a rotation of 53.4° to the right (clockwise, or plus) in water solution at 20°C using the sodium D line as the light source. Substances in solution that rotate light to the right are designated *d* and called dextrorotatory; substances rotating light to the left are designated *l* and called levorotatory.

In 1848, Louis Pasteur (1822-1895), working with the sodium ammonium salt of optically inactive racemic acid, an acid isolated from winery sludges, made a remarkable discovery. On recrystallizing the salt in a cool room, he found that it separated into two crystalline forms, differing only in that they had hemihedral faces inclined in opposite directions. He found that a solution of those crystals having right-handed faces was dextrorotatory, while the left-handed crystals gave a levorotatory solution. A mixture of equal parts of both crystals was optically inactive, as the original acid had been. The *d* crystals were shown to be identical with the then-known *d*-tartaric acid, while the *l*-acid was a new compound. This was the first separation of such a *dl* mixture, and such mixtures are now called *racemic* for this reason. J. Wislicenus (1835-1902), in 1873, working with the naturally occurring *d* and *l* lactic acids, showed that the two optical isomers have identical physical and chemical properties, except for the direction of rotation of polarized light. If the *l* form has a rotation of -3.3° then the *d* form will have a rotation of $+3.3^\circ$.

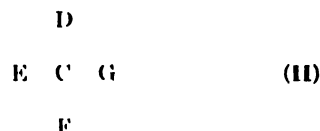
These results were puzzling to the organic chemists of the time, because they did not have a three-dimensional concept of molecular structure. It was the brilliant postulate of the tetrahedral carbon atom, arrived at independently in 1874 by

Jacobus H. van't Hoff (1852-1911) and J. A. Le Bel (1847-1930) that solved the problem and made the existence of optical isomers seem reasonable. The postulate that the four valences of carbon point to the corners of a regular tetrahedron implies that optical isomers can exist, and their well authenticated existence can be taken as evidence for the postulate.

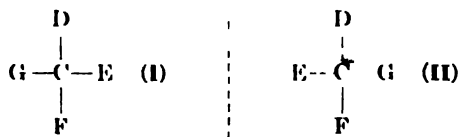
Consider the molecule formed of carbon and four different atoms or groups D, E, F, G



Now, keeping the line DCF fixed, rearrange the other two groups to get



It can be readily seen that the two molecules are related to each other as right and left hands, they are mirror images, but not superimposable if left in the plane of the paper.

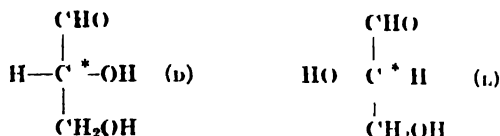


It must be added that they can be superimposed simply by rotating structure II 180° about the axis DCF. This is a fault of the planar representation of a three-dimensional atom. If a model of the two atoms is constructed in the proper manner, it can be seen that they can in no way be superimposed. In considering whether two optical isomers are identical from their planar projections, it must be remembered that rotations of any kind in the plane of the paper are allowed, while lifting the projection off the paper and inverting it is not allowed. Compounds related to each other as the two model compounds (image-mirror image) are called *enantiomorphs* or optical antipodes.

Carbon atoms with four different groups attached to them are called asymmetric carbon atoms, and in chemical symbolism are quite frequently marked with an asterisk (*). It is possible for a compound to have more than one of them. Tartaric acid has two, while naturally occurring compounds such as proteins, with one asymmetric carbon per peptide unit, may have millions. Tartaric acid, with two asymmetric carbon atoms, has a possibility of having four optical isomers, of which three are known.

In order to consider asymmetric compounds without writing out a complete formula each time, a conventional way of writing the planar projection has been adopted. The molecule is represented with the carbon atoms in a line, with the groups

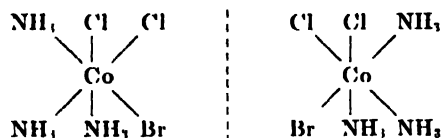
falling to the right or left as if one were sighting down the length of the carbon chain. As a further guide, the configuration of the first carbon atom in the chain is referred to one of the two glycer-aldehydes.



Compounds that have the same configuration as D-glyceraldehyde are designated D, and those with other configuration L. It must be added that configuration as represented in a structural formula and direction of rotation are not necessarily related. D-Glyceric acid is dextrorotatory, while D-lactic acid is levorotatory.

With three, four, and more asymmetric atoms in a molecule, the number of possible isomers becomes tremendous. The maximum number of isomers for n asymmetric atoms is 2^n , but the actual number may be less because of mesomeric pairs. Compounds having the same configuration on all but one carbon atom are called *epimers*. Epimers are quite frequent in the hexoses—6-carbon sugars that have four asymmetric carbon atoms. All the 16 possible optical isomers are known in this series.

Asymmetry of this kind is not, however, limited to carbon compounds. Any atom with tetrahedral or octahedral valences may be asymmetric. If three different groups are present in the octahedral coordination sphere of cobalt, it can be seen that mirror images and optical isomers will exist.



Asymmetric atoms of sulfur, tin, nitrogen, selenium, and other elements have been observed in compounds of those elements.

Asymmetry has been a very useful tool in the detailed study of organic reactions. The question of which bond is broken in the hydrolysis of an ester was one of the first questions to be solved by using pure optical isomers. Recently, other methods, such as radioactive tracer studies, have become mentioned frequently in questions of mechanism, but they are still at best useful supplements to the classical methods of stereochemistry.

ELBERT C. WEAVER

Cross-references: Optical Rotation, Polarimetry, Stereochemistry

ATMOSPHERIC POLLUTION, see AIR POLLUTION

ATOMS

The word "atom" is used universally in chemistry and physics to denote the smallest particle of

an element which can exist either alone or in combination with other atoms of the same or of other elements. Breaking up an atom of an element would give us something which did not have the properties of the given element. The size of an atom is about 2 or 3×10^{-8} cm. Atoms are the building blocks from which molecules are constructed and they are the particles which occupy regularly spaced positions in the lattices of crystals. The mass of the lightest atom, the hydrogen atom, is 1.67×10^{-27} kilogram. This means that its mass is about 1840 times the mass of an electron.

Historical Development. The name "atom" was derived from the Greek word "atomos" which means uncut or indivisible; the Greek philosopher, Democritus, was the first to propose the existence of such elementary particles. The idea was revived late in the nineteenth century in an effort to explain experimental results. Dalton's Law of Partial Pressures showed that in any mixture of gases or of vapors or of both, each constituent exerted its pressure as though the other constituents were not present. Other studies, such as the development of the Kinetic Theory of Gases and measurements on the combining weights of elements, brought out a more complete atomic theory. In many experiments atoms behaved as though they were tiny solid spheres, in accordance with the ideas of Democritus. However, later developments indicated that the atom was anything but solid and indivisible and further that it had associated with it a wave motion. These results showed that the atom was far more complex than a simple solid particle.

Many important discoveries in the last half of the nineteenth century had a direct bearing on beliefs about the structure of matter. Studies of electrical discharges through gases and in particular of cathode rays led to the discovery of electrons, and J. J. Thomson and others showed that electrons are constituents of atoms. Later, Lord Rutherford carried out elaborate experiments on the scattering of radioactive emanations as these particles passed through metal foils. The results convinced him that the positive charges in matter were concentrated in very tiny regions whose size was about 10^{-12} cm. or a millionth of a millionth of a centimeter. This positively charged core or nucleus was surrounded by an equal amount of negative charge.

The Orbital Model. Albert Einstein invoked the idea of light quanta. This theory proposed that the emission of light energy occurred in certain discrete amounts called quanta or in even multiples of these amounts, but not in other amounts. The Danish scientist, Niels Bohr, tied this concept to processes in individual atoms by developing his orbital model of the atom. He postulated that the negative charge in the atom was carried by electrons which rotated in stable orbits around the positive core or nucleus of the atom. His hypothesis for the hydrogen atom was that there was one stable orbit for the single electron which rotated about the nucleus of this atom. The angular momentum of the electron in this orbit was assumed to have a value equal to $h/2\pi$ where h was the universal constant known as Planck's con-

stant. Bohr also assumed the existence of other orbits in each of which the angular momentum was an integral multiple of $h/2\pi$. If the electron should get out into one of these orbits the atom was in an excited state which was not a stable configuration. All other orbits were considered to be impossible arrangements.

This meant that the atom could exist (at least temporarily) in states in which it had certain definite amounts of energy, but states corresponding to electrons in other orbits or other amounts of energy were ruled out. Hydrogen atoms which were not combined into molecules were found in electrical discharges and in the discharges the excited states corresponding to electrons in other than stable orbits also appeared. When an electron dropped from one orbit to one in which it was closer to the nucleus, Bohr's theory stated that energy was emitted and the atom lost this same amount of energy. Since only certain orbits were considered possible, only certain definite amounts of energy were emitted and these amounts corresponded to Einstein's "packets of energy". Also, energy could be absorbed by the atom in amounts equal to the amounts needed to move the electron out to specific orbits.

Atoms of elements other than hydrogen have more than one electron and these are found in specific orbits when the atoms are in their normal states. Each element is characterized by the number of electrons which makes up its normal complement. This number is also equal to the amount of positive charge which is contained in the nucleus when that amount is expressed in multiples of the charge on one proton. These numbers, which are called atomic numbers, range up to 101 which corresponds to the element mendelevium. For each kind of atom there are certain stable orbits and others which correspond to excited states of the atom. If an atom has either more or less than its normal complement of electrons in orbits around it, the atom is said to be ionized.

Extensions of Bohr's model were proposed which used elliptical orbits or shells of negative electricity to account for the results of some precise experiments. None of these have been entirely successful and Bohr's theory is not considered to be a complete picture of the atom. None the less, the model has retained its usefulness because it provided a picture of the atom which could be visualized and the model is frequently used to describe the conclusions reached by theoretical calculations based on much more complicated models of the atom.

Atomic Weights. The masses of atoms are often expressed as "atomic weights". The atomic weight of an atom is the average mass of the atoms making up a sample of the element when these masses are expressed on a proportional scale on which the average mass of the atoms of a sample of ordinary oxygen is taken as exactly 16. On such a scale, hydrogen has an atomic weight of 1.008. When using this scale, the whole number or integer nearest to the mass of a particular atom is called the mass number of that atom.

Classification of Elements. Since all the atoms of any one element have the same amount

of positive charge on each of their nuclei and this amount is different from the amount on the nuclei of any other element, the elements can be arranged in order of increasing positive charge. When this is done, it is found that these amounts are all even multiples of the charge of the first element on the list—hydrogen. Each element is assigned an atomic number which denotes its position on this list. This number also indicates the number of electrons in the orbits about the nucleus. The arrangement of the electrons, particularly the number of electrons in the outermost orbit which is occupied, determines the way in which the atom will combine with other atoms to form molecules. In an attempt to classify elements, Mendeléeff found that they could be placed in groups such that those in any one group had similar chemical and physical properties and that various properties showed a continuing trend throughout the group. Names of the elements can be arranged in rows with atomic number increasing from left to right, starting a new row whenever an element is reached which is similar to hydrogen in its chemical properties. This results in a periodic chart of the elements similar to the one proposed by Mendeléeff. Elements which are in any one column are those which are similar in their chemical properties. These characteristics are determined mainly by the number of electrons in the outermost orbit which is occupied.

Electron Distribution. The electrons in any atom fall into groups or classes in accordance with the amount of energy needed to remove them from the atom and these groups are called the K shell, the L shell, the M shell, etc. Experiments with x-ray photons are used to determine the energies necessary to remove electrons. For each kind of atom the electrons which are hardest to remove are the K electrons, those in the next group are L electrons, etc. The maximum number of electrons in each shell is 2 for the K shell, 8 for the L shell, 18 for the M shell, and 32 for the N shell.

If a start is made with the lightest atom, the hydrogen atom, and each element is considered in turn throughout the Periodic Table, we find that more and more orbits are occupied. The second element, helium, has two electrons for each atom and these fill the K shell. The next atoms have some electrons in the L shell. It is not always found that any given shell is filled before the next shell receives any electrons. Sometimes a shell is partially filled to a convenient semi-complete stopping place with 8 or 18 electrons in the outermost occupied orbit. Then in the following elements some electrons are placed in the next orbit before any more are placed in the semi-complete orbit. Later, this orbit is filled in. When the outermost orbit which is occupied is full, the atom is inert. There are also inert atoms when the M shell reaches its semi-complete point with 8 electrons and when the N shell has 18 electrons.

The atoms of elements just beyond the inert ones have one and only one electron in the outermost shell which is occupied. This last electron revolves in a field which is similar to that of the one electron of the hydrogen atom. This results in these elements having spectra which are similar

to that of hydrogen, and these atoms all have similar chemical properties. Throughout the Periodic Table there are correlations between the chemical properties and the number of atoms in the outer orbit.

One might expect that the atoms which have several occupied shells would be considerably larger than those which have fewer occupied shells. However, the larger attractive forces, which the more strongly charged nuclei of these heavier atoms exert on the electrons, result in the stable orbits being drawn inward so that there is only a comparatively slight variation in size among all the known atoms.

The Nucleus. The nucleus or core of the atom contains all the positive charge associated with that particle. For a long time it was believed that nuclei consisted of protons and electrons. This gave way to the belief that nuclei consisted of protons and neutrons. Elements differ from each other in the number of protons in their nuclei. The lightest element, hydrogen, has only one proton in each nucleus. The next element in the Periodic Table, helium, has two, and so on throughout the table. In addition to the protons present all atoms, except some of those of the very lightest elements, contain one or more neutral particles or neutrons. A neutron has almost exactly the same mass as the proton but differs in that it is uncharged.

It is possible for two atoms to contain the same number of protons in their nuclei and thus be atoms of the same element, but to have different numbers of neutrons and thus have different atomic masses. Such atoms are called *isotopes*. Some elements are known to exist in as many as seven or eight isotopic forms. The mass number of an atom of a particular isotope can be obtained by adding the number of neutrons in its nucleus to the number of protons in that same nucleus. Different isotopes of an element may differ widely in the stability of their nuclei.

The way in which the components of a nucleus (the nucleons) are arranged is at the present time the object of much study. One hypothesis is that these particles are in much the same form as they are when existing separately but are closely packed together in the atom. Another theory states that they exist more in the form of shells one inside the other. The nucleus is held together by forces which are extremely great when the separations are very small, but which fall off very rapidly as the distances between particles increase. The Japanese scientist, Yukawa, developed a mathematical meson theory which deals with these forces.

The nuclei of all the very heavy elements are unstable in varying degrees and decay spontaneously with the emission of radiations. This process, called *radioactivity*, was first discovered by Becquerel; it transforms an atom of one element into an atom of another element, the disintegrations following statistical laws. Some isotopes decay so slowly that it takes thousands of years for one-half of the atoms of a given sample to decay and another equal period of time for one-half of the remainder to disintegrate. Others decay so rapidly

that one half of the atoms in a given sample will decay in a tiny fraction of a second. Some isotopes of the lighter elements are also radioactive. The half life for radioactive decay is the length of time it takes for one-half of the atoms in a given sample to decay. At least one radioactive isotope of every element has been found to occur naturally or has been prepared artificially.

Theoretical Interpretation of the Atom: Powerful mathematical methods give quantitative treatments of atomic and subatomic processes. These theories are called quantum mechanics or wave mechanics and are primarily the results of investigations by Heisenberg, Dirac, and Schrödinger. The background for these theories comes from Louis de Broglie's realization that the circumference of the circular orbit of Bohr's atom model for hydrogen in the normal state is equal to the wavelength of the waves which can be associated with the moving electrons. This leads to the idea that in the atom there is a standing wave associated with the electron as it moves in its orbit. Erwin Schrödinger proposed that this wave length be substituted in a classical wave equation and from this beginning he derived a wave equation for the hydrogen atom. This pictures the negative charge of the electrons as a standing wave about the nucleus. The square of the amplitude of the wave represents the probability that the electron can be found at that point.

For other atoms wave mechanics indicates a method for finding the energy values and the electron distributions for stationary states of the atoms. The mathematical difficulties, where many particles are involved, are stupendous, but successes are being achieved. This development is generally known as the modern orbital theory of atomic structure.

Atomic Energy. Much is being written at the present time about atomic energy, using the expression to refer specifically to the energy obtained from certain changes in nuclear structure. The foundation of this idea of obtaining energy in usable form from atoms can be traced to Albert Einstein who showed that matter seemed to be a form of energy and that it could be changed to other forms of energy. The amount of energy obtained is given by the equation $E = mc^2$. The energy E is given in ergs if m is the mass in grams and c is the velocity of light in centimeters per second. One gram would correspond to 9×10^{20} ergs. At the present time only a small fraction of the mass of any given sample can be converted, but this fraction still yields a vast quantity of energy.

Considering two atoms of deuterium, the heavy hydrogen isotope, each nucleus contains one proton and one neutron. At high temperatures and high pressures these will combine into one nucleus. This new nucleus has two protons and two neutrons. Thus, it is an atom of helium. However, if we add up the masses of the starting atoms very carefully and compare the sum with that of the helium nucleus, we find that a small amount of mass is missing. It has been converted into other forms of energy. The loss of mass is often referred to as "mass defect".

Considering any other combinations of very

light nuclei which result in heavier nuclei, we find that some mass is lost in the process of *fusion*. This mass appears as some other type of energy. On the other hand, if we consider the heaviest atoms in the Periodic Table, we find that they can be broken into two nearly equal parts plus some very light particles. The sum of all the masses of the resulting particles is less than that of the original materials. This process is called *fission*, and again we have the conversion of mass into other forms of energy.

Chain reactions occur when some of the particles produced in the fission process are ones which are capable of breaking other atoms, and the geometry of the arrangement is such that there is a great enough chance of their breaking other atoms before they are absorbed by competing processes, or are lost outside of the mass of fissionable material, or are slowed down to the point where they can no longer trigger the fission process.

Atoms should be thought of as entities which are very small but none the less so complex that they stagger the imagination and offer rich fields for further research and speculation.

ROBERT M. BENANCON

Cross-references: *Molecules, Protons, Electrons, Elements, Radioactivity, Periodic Law, Nuclonics*

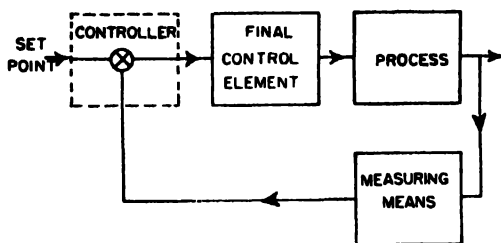


Fig. 1a. Control system block diagram

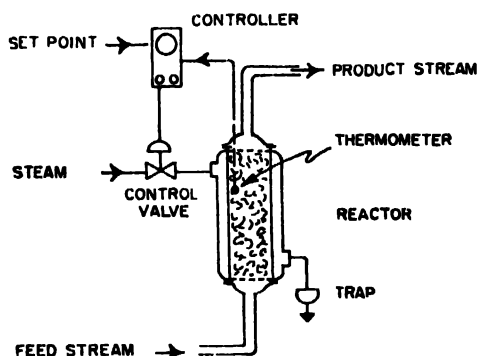


Fig. 1b

AUTOIGNITION POINT

The autoignition point of a substance, whether solid, liquid, or gaseous, is the minimum temperature required to initiate or cause self-sustained combustion independently of the heating or heated element. The figures on ignition temperature may vary, depending upon the test method, as it varies with the size, shape and material of the testing container and other factors. Some typical ignition temperatures are the following: acetone 1000°F, amyl acetate 750°F, aniline 1000°F, butane 808°F, carbon disulfide 212°F, ethyl ether 356°F, phenol 1319°F, toluene 1026°F, white pine shavings 507°F, cotton batting 446°F, magnesium powder (fine) 883°F, nitrocellulose film 279°F.

C. I. BABCOCK

AUTOMATIC PROCESS CONTROL

The spectacular and continuing growth of the chemical process industries has been due in part to the adaptability of chemical and allied processes to automatic regulation. All control systems may be represented as loops of varying complexity. The most useful representation of the control loop is the *signal flow diagram*, which is like a process flow sheet except it identifies the flow of information rather than the flow of materials. It is frequently called a *block diagram*, since the individual loop components appear merely as blocks.

Figure 1a shows a simple control loop containing the basic elements of *measuring means*, *controller*, *final control unit*, and *process*. The particular system represented might be a temperature control system for a chemical reactor, shown in Figure 1b,

wherein a catalyst bed temperature is sensed by a thermometer which causes a conventional controller to position a steam valve. In this example, the steam-heated reactor would comprise the process.

It is apparent that the system of Figure 1 is a *closed-loop system* inasmuch as the response of the process is fed back via the controller to the final control element. Thus *feedback* is a characteristic of closed-loop control. With such control systems the results of control action are always under scrutiny and the control can be highly effective.

It is also possible for the control system to be an *open-loop* one. In the example of Figure 1b, the reactor temperature could be controlled by setting the steam valve manually in accordance with past experience, rather than in accordance with the measured temperature. Obviously for such a system to work, a close calibration between valve position and reactor temperature would be necessary in addition to virtual freedom from external changes. For most processes open-loop control systems are impractical.

Control Variables. In Figure 1a the measuring means is shown taking an output signal from the process and relaying it to the controller. The process output is the *controlled variable*, which might be temperature, pressure, flow rate, liquid level or composition. Other possible variables are of less importance in process control.

In general the best variable to control is the one which most sensitively reflects the behavior of the process. Often the variable being measured and controlled is not the variable for which the control is desired. For example, in a reactor the important controller may maintain a constant temperature at a particular point in the catalyst bed, yet the actual quantity being controlled is

the product stream composition. A recent trend has been to base the control on the actual variable to be optimized. Such control is called *end-point control*, particularly in cases where product quality is the actual variable to be regulated.

Regardless of the variable being measured, the kind of signal which is most useful to controllers is either a mechanical motion or an electric signal of some sort.

Controllers. Controllers may be classified according to their drive as electric, pneumatic or hydraulic. All three types are found in the process industries; pneumatic and electric instruments are most widely used in that order, and hydraulic controls are used much less frequently. Pneumatic instruments are generally preferred in the petroleum and similar industries where fire hazards make electrical devices dangerous unless specially protected.

Regardless of the type of controller drive, the same general modes of control may be generated by each. The important modes for process control are:

1. On-off or two position control
2. Proportional-speed floating control or integral action.
3. Proportional control.
4. Derivative or rate action.

Various modifications are available such as three-position and single-speed floating control but these are relatively unimportant. Some of the modes are used together as described below.

Two-Position Control. The least expensive and most widely used control mode is two-position control. If the controlled variable lies below the *set point*, i.e., the value to be maintained by the controller, the output signal from the controller may cause a valve to open fully, and if the variable lies above, the valve will close. This type of control is characteristic of household heating systems. It finds use in the process industries for simple operations where moderate cycling of the variable is tolerable.

Integral Control. Proportional speed floating control derives its name from the fact that the rate of change of the controller output is proportional to the *deviation*, which is the difference between the variable and the set point. In other words, the controller output is proportional to the integral of the deviation, hence the name integral control. At the present time integral action is most often used in conjunction with proportional control.

Proportional Control. In proportional control the controller output is proportional to the deviation. This type of control is basic for most controllers applied to processes in which cycling of the controlled variable is undesirable (See *Instrumentation*.)

Automatic Reset. The gain (ratio of output to input) of a proportional controller is usually set at one-half the gain required to cause sustained oscillation in the controlled variable. However, if this setting results in too low a gain, the controller will tolerate large deviations or *offsets* in the controlled variable for various load conditions in the process. Offsets may be eliminated by

adding integral action to the proportional action. The proportional control provides strong and immediate corrective action, and the integral action assures continuing additional corrective action until the deviation has disappeared. This combination of control modes is called *proportional plus integral* or *proportional with automatic reset*.

Derivative Action. Although not a control action by itself, derivative action or rate action causes an anticipatory correction by making the controller output proportional to the derivative or rate of change of the deviation. It resists sudden changes in the variable and by this stabilizing action, it permits the use of high gain proportional action.

Three Mode Control. Derivative control must be used with proportional control either alone or in combination with integral action. The latter case is called *three-mode control*, and is used for hard-to-control processes where neither offset cycling, and excessive overshooting of the variable following a disturbance is tolerable.

Final Control Elements. The output from a pneumatic controller is an air pressure and from an electric controller is a voltage. In process control these outputs most usually are applied to valve motors, such as diaphragms or reversible electric motors, to position valves in the various process flow streams. In some cases the controller output is applied indirectly through a *valve positioner*, which is a servomechanism designed to fix the valve position at exactly that commanded by the controller.

Control Systems. For many processes it is advantageous to couple controllers in various ways. *Ratio controllers*, for example, maintain a fixed proportion between two or more process streams. In *cascaded* control systems, the output of the master controller fixes the set point of an auxiliary controller. Such a system might be used in a cracking furnace where the auxiliary controller would control the flow of fuel to the burners and its set point would be adjusted by the master controller depending on the outlet temperature of the cracked oil at the exit of the cracking coils.

Current Trends. Present trends in process control are toward: increased overall use as reflected in a rising percentage of total plant cost for control instruments; smaller instruments or *miniaturization*; increased localization of controls; point of application to improve control effectiveness and at the same time simplify the central control panel; increased use of graphic panels, wherein the control panel is arranged like a flow diagram of the process under control with instruments located at points on the diagram corresponding to their points of application in the process; and increased use of end-point control. On the theoretical side the trends are toward a more quantitative treatment of control system design.

These trends will continue for the future, along with a new trend toward a tighter over-all integrated control in which magnitudes and emphasis of production will be set automatically by computers operating on basic economic data. This last trend is loosely called *automation*.

Another new trend is the design of instruments to fit special processes such as extremely rapid chemical reactions. The practice for conventional processes in the past and today has been to design the plant and equipment and then add the appropriate standard controls. For new, high speed processes conventional controls may be less economical in the long run than specially designed instruments.

ERNEST F. JOHNSON

Cross-references: *Instrumentation*

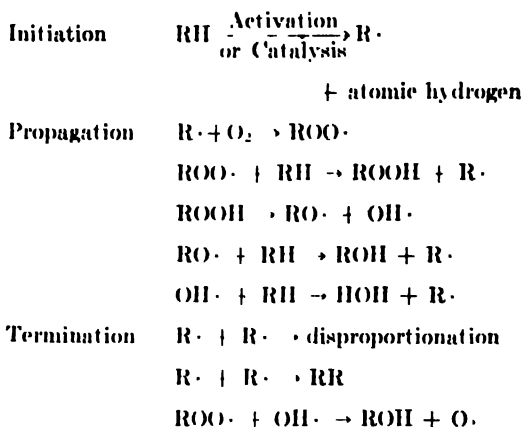
AUTOXIDATION

The term "autoxidation" is applied to those spontaneous oxidations which take place with molecular oxygen or air at moderate temperatures (usually below 150°C) without visible combustion. Autoxidation may proceed through an ionic mechanism, though in most cases the reaction follows a free radical-induced chain mechanism. The reaction is usually autocatalytic and may be initiated thermally, photochemically or by addition of either free radical generators or metallic catalysts. Being a chain reaction, the rate of autoxidation may be greatly increased or decreased by traces of foreign material.

Most organic and a variety of inorganic compounds are susceptible to autoxidation. The mild conditions under which many compounds react with oxygen presents a serious problem of deterioration though, on the other hand, autoxidation offers wide possibilities in the field of synthetic chemistry. Several industrial processes such as the manufacture of *o*-phthalic anhydride from naphthalene and more recently of phenol and acetone from cumene are based on autoxidation. In the paint industry many of the finishes employing drying oils are dependent on autoxidation as well as polymerization for their durable qualities. The reaction has found limited use in development of analytical techniques.

Degradative processes involving autoxidation are very numerous. The rancidity developed by edible fats and oils on standing in the presence of air is due to autoxidation, with formation of acidic products. Gum formation in lubricating oils and fuels may be attributed largely to autoxidation, as may the deterioration of many polymers, especially on exposure to sunlight. In the field of metallurgy the corrosion of certain metals may be considered in part an autoxidative process.

The chemistry of autoxidation has been studied extensively in the hydrocarbon field and the mechanism elaborated for this class of compounds shown to be characteristic of free radical type autoxidation. At temperatures of 100°C or less or on exposure to ultraviolet light at lower temperatures many hydrocarbons react with oxygen rapidly to produce a variety of products. It is now generally agreed that reaction is initiated by removal of hydrogen from a molecule of the substrate to form a free radical, R·. The following steps represent the overall reaction in its simplest form.



Kinetic studies with tetralin have shown that formation of hydroperoxide is almost quantitative with respect to oxygen absorbed in the initial stages of reaction. After a critical concentration is reached, homolytic cleavage of peroxide commences and the resulting RO· and OH· radicals may then initiate new chains—this is the autocatalytic phase of the reaction. In the case of aldehydes it has been shown that peracids rather than hydroperoxides are the first products of reaction; though the peracids do attack the aldehyde, reaction is through a heterolytic mechanism and hence these autoxidations do not become autocatalytic.

Ease of removal of hydrogen to form free radicals is a function of molecular structure. Groups such as carbonyl, carboxyl, phenyl or the ethylenic double bond activate hydrogen on adjacent carbon atoms so that autoxidation occurs more readily when these groupings are present in the molecule. Thus olefins are more susceptible to autoxidation than paraffins. Autoxidation may be inhibited by addition of antioxidants (HA) which are attacked by the propagating radicals breaking the oxidative chain:



An effective antioxidant must form a radical (A·) which is incapable of chain propagation. In this way autoxidation is inhibited as long as unreacted antioxidant is available. In contrast, addition of foreign peroxides or other generators of active free radicals affords a source of additional radicals capable of initiating autoxidation or increasing the rate. Also metals having variable valence, such as copper, cobalt, manganese etc. can promote autoxidation through catalytic decomposition of hydroperoxides.

W. LINCOLN HAWKINS

Cross-references: *Antioxidants, Oxidation*

AUXILIARIES

Textile auxiliaries are the chemical processing aids or assistants employed in the preparation and finishing of both natural and synthetic fibers and fabrics. While the manufacture of textile fabrics is primarily a series of mechanical opera-

tions, certain chemical treatments are necessary in the processing, either to assist the mechanical operations or to protect the fibers or yarn from damage. Auxiliaries may also be used to improve bleaching, dyeing, printing or finishing, the hand, quality or appearance of goods, or to increase the efficiency of the various processes. They can roughly be divided into the following categories:

(1) Fats, oils and waxes, natural and synthetic, which serve primarily as lubricants and are generally combined with other auxiliaries.

(2) Starches, gums and glues, which serve as film-forming coatings, thickeners and adhesives in a wide variety of compositions.

(3) Surface-active agents, including soaps, which are used not only as detergents but also as assistants in a number of processing steps.

(4) Acids, alkalis and various inorganic chemicals, which are used in operations such as bleaching, carbonizing, oxidizing, flame proofing, etc.

(5) Solvents and other organic chemicals used in many processing operations; this is somewhat of a catch-all class.

(6) Finishes of various types, including resin and cellulose finishes and the various repellent, protective and decorative finishes.

In a sense, water is the most important of the textile auxiliaries, for without it textile processing as we know it could not exist. The majority of textile processing assistants must be water-soluble, not only because of the ease and economy of application but also because it is easier and cheaper to remove them when their job is done. Water softeners, organic and inorganic, corrosion inhibitors, thickeners, and even some of the germicides and fungicides are classed as textile auxiliaries primarily because they make water more suitable for use in the various preparatory, dyeing and finishing operations.

The need to protect the fibers and yarns from mechanical abrasion naturally increases as the speed of the machines increases. Today, oils, fats and waxes are identified with textile processing at almost every stage of production from yarn spinning to fabric finishing. They are employed as fiber, yarn and machine lubricants and are formulated into batching oils, coning oils, spinning oils, throwing oils, plasticizers, softeners, size compounds, coatings and water repellents. As chemical raw materials they are used as bases in the synthesis of new surfactants, antifoaming agents, antistatic agents, soaps, softeners, resins, dyes, permanent finishes and even in making synthetic fibers. As "oils", their chief function is to lubricate or to impart lubricity to various compounded auxiliaries. Mineral oils and waxes are commonly classified with the naturally occurring oils, fats and waxes for most textile uses, though they cannot be removed as readily from textiles and have obvious differences in chemical reactivity.

Soap is one of the oldest textile auxiliaries and the forerunner of modern synthetic surface-active agents. These, also variously described as wetting agents, detergents or syndets, dispersants, emulsifiers and "soapless soaps", are what most people have in mind when they refer to textile auxiliaries. They are employed as assistants in numerous proc-

essing steps, such as wetting and rewetting, scouring and dyeing. They are utilized as antistatic agents, aftertreating agents for dyeing, bleaching assistants, carbonizing assistants, corrosion inhibitors, crabbing assistants, degreasing and dispersing agents, dyeing assistants and retardants, emulsifying and finishing agents, germicides and antiseptics, kier boiling and scouring aids, lubricants, mildew preventatives, plasticizers, protective agents for wool and silk in wet processing, softeners, stripping assistants, and in the formulation of coning oils, spin finishes, fabric finishes, fulling soaps and thickeners, just to mention some of their better known uses. Examples include such internationally known products as the "Igepons", "Igepals", "Nacconols", "Duponols", "Tritons", "Nopeo" oils, "Aerosols", "Teepols", "Deccrosols", "Aveconit", "Spans", "Tweens", "Orthner Compound", "Ultrawet", etc.

Starches, gums and glues are also textile auxiliaries of long standing. Like the oils and fats, they are obtained from rather abundant natural sources all over the world. They function chiefly as adhesives and film-formers in textile processing. Throughout their centuries of usage in various operations, such as sizing, coating, and print-paste thickening, they have been modified physically and chemically to satisfy the multitude of different ideas on how their basic properties can best be utilized. Starches and gums are derived from plants and are complex carbohydrates, whereas animal glues and gelatins, derived from animal tissues, are proteins. The various synthetic glues and gums, like hydroxyethyl cellulose, as well as other types of adhesives, such as casein, fish and vegetable glues, are of much more recent origin.

The principal auxiliaries used in the preparation of warp sizes for imparting strength and abrasion resistance to yarns for weaving include starches, gums, glue, gelatin, casein, polyacrylic acid, polyvinyl alcohol, tallow, oils, waxes, synthetic resins, preservatives, enzymes and defoamers. The starches have long been considered the most economical film forming and binding agents for sizing yarns made from natural fibers. Glue and synthetic sizing materials such as polymethacrylic acid are more commonly used on rayon and the newer synthetic fibers. The water-absorbing properties of the gums, the lubricity of tallow and the thinning action of certain enzymes are normally utilized in formulation of many slashing or sizing compounds.

The functions of finishes are diverse, as are the materials used. After dyeing, almost all textile materials are subjected to some sort of finishing operation, mechanical or chemical or both, to eliminate wrinkles, cracks and other imperfections induced by wet processing; to set, compact and fix their structures; and frequently to modify their physical and chemical characteristics. Mechanical operations such as calendering, napping and embossing help eliminate distortions and wrinkles, produce stabilization of cloth structure and may impart a characteristic new feel to fabrics. Products such as softeners and dullers are used to accentuate or inhibit some natural physical or

chemical characteristic of a fabric. Various natural and synthetic resins are employed to mask weaving and knitting defects and imperfections, and to increase the life and durability of a textile. The shape, structure and form of a material can be maintained or altered to give new characteristics by use of such auxiliaries as antislip and shrink-resistant resins and sizes, mothproofing, flameproofing and water-repellent compounds.

Combinations, physical mixtures of various types of chemicals and auxiliaries, specialized modifications resulting from the use of heat or chemical agents are so numerous that they are often more logically classified as "formulas." Yet they form part of the thousands of chemical products sold to and used by textile mills as textile auxiliaries.

HENRY C. SPEEL

AVOGADRO (1776-1856)

Avogadro, a native of Turin, Italy, held the chair of higher physics at Turin University for many years. In 1811, he published obscurely the principle that bears his name: "Equal volumes of gases at the same temperature and pressure contain the same number of molecules." This law, apparently derived by intuition, was Avogadro's attempt to explain the laws of Boyle, Charles, and Gay-Lussac. It was not generally appreciated until 47 years later when Cannizzaro (*q.v.*) recognized its value. Avogadro's law applies strictly to an "ideal" gas. Gases that are easily liquefied deviate from it somewhat.

Some consequences of Avogadro's law are: (1) The molecular weights of gases are proportional to their densities: $\text{CO}_2/\text{H}_2 = 1.98 \text{ g per liter}/0.09 \text{ g per liter} = 22/1$; that is, a molecule of carbon dioxide is 22 times heavier than a molecule of hydrogen. (2) By deduction, molecules of oxygen, hydrogen, nitrogen, chlorine, and a few other gases contain two atoms. (3) The gram molecular volume (the volume of a gas that contains one mole expressed in grams) of any gas at standard temperature and pressure is 22.4 liters. For oxygen, molecular weight 32; density 1.43 grams per liter: gram molecular volume = $32 \text{ g}/1.43 \text{ g per liter} = 22.4 \text{ liters}$.

The Avogadro number, sometimes called the Loschmidt (1865) number, may be found in several ways including: (1) calculation from Brownian movement; (2) use of the Langmuir technique, i.e., spreading a drop of oleic acid of known concentration on a clean water surface that is sprinkled with tale, and measuring the extent of spreading; (3) measuring the quantity of electricity equivalent to one electron, and using Faraday's laws; (4) calculating the number of alpha particles and measuring the radon gas evolved in the same interval of time from a radioactive material; (5) displacement of particles in suspensions; (6) x-ray techniques. All methods give reasonably good agreement. The accepted value for Avogadro's number is $6.0228 (\pm 0.0011) \times 10^{23}$ molecules per gram mole. The symbol for Avogadro's number is usually *N*. This constant represents the

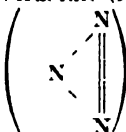
number of molecules in a gram molecular weight (one mole) of a given gas. The constant is used extensively in physical chemistry, especially in calculations that involve molecules of gases. The Boltzmann constant (*k*) is R/N , the gas constant per single molecule. Its value is 1.380×10^{-16} erg per degree.

ELBERT C. WEAVER

Cross-references: *Atoms, Cannizzaro, Gas Laws*

AZIDES

Azides comprise a group of chemicals of characteristic formula $\text{R}(\text{N}_3)_x$. *R* may be almost any metal atom, a hydrogen atom, a halogen atom, the ammonium radical, a complex ($[\text{Co}(\text{NH}_3)_6]$, $[\text{Hg}(\text{CN})_2\text{M}]$ with *M* = Cu, Zn, Co, Ni) an organic radical (e.g., methyl, phenyl, nitrophenol, dinitrophenol, *p*-nitrobenzyl, ethyl nitrate, etc.), and a variety of other groups or radicals. In the inorganic series, and according to most authorities in the organic as well, the azide group has a chain structure ($\text{N}=\text{N}=\text{N}$) rather than a ring structure



All the heavy metal azides, hydrogen

azide, and most if not all of the light metal azides (under appropriate conditions) are explosive. Many of the organic azides are also explosive, especially those containing in addition to the azide group a nitro group ($-\text{NO}_2$). The alkali and alkaline-earth metal azides are the least explosive of the metal azides some of which, e.g., $\text{Ba}(\text{N}_3)_2$, NaN_3 , are incapable of propagating a detonation wave in small quantities but would probably propagate in large charges.

Hydrogen azide (HN_3), the chemical properties of which are indicative of azide chemistry in general, is a very sensitive explosive with a heat of explosion between 1400 and 1550 kg-cal/kg. This heat of explosion is comparable with that of the powerful explosives RDX, PETN and nitroglycerin. Hydrogen azide is a colorless, highly volatile liquid of boiling point 37°C and melting point -80°C . It is a protoplasmic poison resembling in this respect hydrogen cyanide (HCN). Hydrogen azide is soluble in water, alcohols, and ether and is itself a solvent for many substances. In the pure state it shows decomposition at room temperature after four to five days. In aqueous solution (hydrazoic acid) it is stable, but catalyzed by active platinum, it is decomposed into ammonia and nitrogen.

Hydrazoic acid is a monobasic acid with properties resembling the halogen acids. It reacts with acids to liberate nitrogen gas among other compounds and decomposes upon electrolysis with the evolution of nitrogen and hydrogen, probably with $(\text{N}_2)_2$ as an intermediate. It reacts readily with oxidizing agents to give a variety of products one of which is generally nitrogen. It is reduced by the action of reducing agents probably through triazene (H_2N_3) and triazane $[(\text{H}_2\text{N})_3\text{NH}]$ to hydrazine (NH_2NH_2) and finally to ammonia. Tetra-

zene (N_4H_4) may also be produced by reduction of hydrazoic acid. Hydrazoic acid is a powerful nitridizing as well as oxidizing agent.

Sodium azide is important in the preparation of heavy metal azides, principally lead azide. It is prepared in a variety of ways, principal among which are the reactions of nitrous oxide and sodium amide ($\text{N}_2\text{O} + \text{NaNH}_2$) and the alkyl nitride-hydrazine synthesis, both of which have been adapted to laboratory or larger scale production of sodium azide. Solutions of sodium azide react metathetically with soluble copper, silver, lead, mercurous and thallous salts to precipitate the corresponding (insoluble) azides. The soluble metal azides are obtained from hydrazoic acid by metathesis of barium azide with soluble sulfates, or with potassium azide and soluble perchlorates. Ammonium, ethylammonium and diethylammonium azides may be obtained from reactions of solutions of hydrogen azides in ether with the corresponding anhydrobases in ether or alcohol.

Some metal azides, including those of silver, mercury (mercurous), lead and sodium, are sensitive to visible or ultraviolet light, resembling the silver halides in this respect; they are decomposed by light to form the metal and nitrogen. All metal azides are characterized by thermal instability at temperatures starting in the range 100 to 200°C, depending on the particular metal azide. At higher temperatures the heavy metal azides may explode violently. Few if any metal azides are stable at their melting points. The thermal decomposition of the heavy-metal azides is autocatalytic, (q.v.) being promoted by metallic nuclei which form during decomposition, or by the action of light of appropriate wave length following a mechanism similar to that involved in the development of photographic emulsions. The thermal decomposition of metal azides has been used to prepare the corresponding metals in pure form. This method is inapplicable, however, to the alkali metals owing to the relative stability of the alkali nitrides.

In general, the explosive azides, particularly the heavy-metal azides, are very sensitive and may be detonated directly by shock, friction, heat, electrical discharge, and other energy sources. They must therefore be prepared and handled with extreme caution. Their shipment and storage are carefully regulated by law.

The most important commercial metal azide is *lead azide*, used extensively in commercial and

military detonators. Lead azide is one of the most effective (primary) explosives available for use in the "composition detonator" which contains several specialized elements: a bridge wire, an ignition agent, a primary explosive, and a base charge. Application of sufficient current heats or melts the bridge wire, igniting the igniter element, which delivers a hot intensified flame to the primary explosive. The initial combustion reaction is transformed suddenly into a detonation in the primary explosive. The detonation wave formed in the primary explosive is intensified in the base charge.

Mercury fulminate, for many years the most useful primary explosive in detonators, is more easily ignited and develops a greater detonation pressure or priming impulse than lead azide. However, the transition from an explosive deflagration to a detonation takes place more readily in lead azide than in mercury fulminate, especially at high densities where the latter may "dead press." Where the primary explosive itself is required to perform all the functions of a detonator (e.g., an "ordinary" fuse cap) mercury fulminate is apparently unsurpassed. A "composition cap", however, may make use of the most efficient elements for each separate stage of reaction in which few, if any, substances are more suited as the primary explosive than lead azide in all necessary requirements (surveillance, cost, sensitivity, ease of preparation, and effectiveness to carry out the primary purpose of the detonator--the creation of the detonation wave). Other azides have proved either too sensitive and expensive (e.g., silver azide, cadmium azide, copper azide) or too insensitive (e.g., the alkali and alkaline earth azides) to replace lead azide as the primary explosive in a "composition detonator". Lead azide is, however, not without its limitations, one of which is the tendency in the presence of moisture to attack copper and brass to form the extremely sensitive cuprous azide. Modern detonators based on lead azide, however, are designed effectively to overcome some of the undesirable properties of lead azide. Even the extreme hazards of the detonator have been minimized by ingenious design of the "composition cap", but a detonator remains a highly hazardous device and should be handled cautiously at all times.

M. A. COOK

Cross-references: *Explosives, Nitrogen Compounds*

B

BABCOCK (1843-1931)

S. M. Babcock was born at Bridgewater, New York, October 22, 1843 and died in Madison, Wisconsin, July 2, 1931. On October 27, 1896, he was married to Mary Crandall but no children were born of this union. He took his A.B. degree at Tufts College in 1866 and his Doctor's degree at the University of Gottingen, Germany, in 1879. From 1875 to 1877 and from 1881 to 1882 he was instructor in Chemistry at Cornell University. From 1882 to 1888 he was chemist at the Agricultural Experiment Station in Geneva, New York. In 1888 he became professor of Wisconsin and chief chemist of the Wisconsin Agricultural Experiment Station. He became assistant director of the Station in 1889.

He was one of the early students to study the biological aspects of chemistry in a German university and he brought back to this country many basic ideas which have been useful for many decades. At Gottingen he studied under Huebner, the successor to the great chemist Wohler. When Babcock was in the laboratory, Wohler was still alive and paid him a daily visit there. On one occasion he showed Babcock a sample of the first urea that was synthesized and a bit of iodine that was sent by Courtois in Paris to Wohler. Babcock also visited Bunsen at Heidelberg and was greatly impressed by the simplicity and originality of that great chemist. When Babcock returned to the United States he was one of the first to introduce the Kjeldahl method for the estimation of nitrogen and protein in biological materials.

In the popular mind, Babcock will be remembered longest for his invention of the milk fat test which bears his name. This was done in 1890, two years after he arrived in Wisconsin and when he was 47 years old. He emphasized a number of times that his real contribution to the development of the milk test lay in his introduction of the centrifuge as a part of the test, thereby shortening the time of operation. Here again, his fundamental knowledge of physics stood him in good stead. He also developed a viscosimeter, the construction of which in principle is the basis of the modern viscosimeter. Another important piece of work contributed by Babcock was his solution of the problem of metabolic water, a fundamental question in plant and animal physiology.

During his early work at Geneva Agricultural Experiment Station Babcock lost faith in the ability of the prevailing method of food analysis to give valuable information about the nutritive value of a foodstuff. When he came to Wisconsin, he put his ideas to work and showed that cows fed

rations which were alike according to conventional methods of food analysis and energy content, but selected from different sources, produced marked differences in milk production and behavior of the animals. His notes were incomplete and were never published, but this work was the forerunner of the development at Wisconsin of the newer approach to nutrition, and was probably the first experiment used in testing the biological values of different foodstuffs.

During the latter part of his life, much time was spent in the field of physics, especially on the constitution of matter. Even in his earlier years he had given much thought to this subject and had formulated in his own mind an hypothesis that departed radically from the commonly accepted ideas concerning the relation of matter and energy. Many experiments were conducted with apparatus that he constructed with his own hands. During the latter years of his life, he attempted to summarize all these data into book form but the unfinished manuscript remained at the time of his death. Many have expressed the opinion that the basic principles now recognized in the new science of physics were foreshadowed in the bold postulates that Babcock set forth in his studies.

C. A. ELKHJEN

Cross-references: *Biochemistry, Nutrition, Milk*

BACTERIOLOGY

As the name implies, bacteriology is the science dealing with the nature, growth and treatment of bacteria. Bacteria are typically tiny, sometimes ultramicroscopic organisms, which are frequently motile. Recent methods (electron microscope, infra-red beam, chemical tests) indicate the presence of nuclear material or chromatin (desoxyribonucleic acid, etc.); but the behavior of the nuclear material seems somewhat simpler than that seen in larger cells. Typical reproduction is by binary fission, after which the cells may separate or else cling together in chains or masses. Shapes vary greatly—spheres, straight, curved or spiral rods, often with flagellae. Resistant spores are also formed by certain species. Bacteria are free-living, generally saprophytes or parasites, and some are pathogenic for man, animals and plants.

During the last century, bacteriological discoveries and applications have greatly lengthened the average life of man by continually advancing the understanding and treatment of diseases and disease prevention. As knowledge developed about bacteria and other microorganisms and the chemical changes directed by their biocatalysts (enzymes), virology, immunology and microbiology

emerged and became useful and highly specialized sciences.

Anton Van Leeuwenhoek, with his home-made microscopes, first observed microorganisms ("little animals", he called them), and in 1676 saw and drew pictures of bacteria in pus. But it was nearly two centuries before anyone saw the relationship between this observation and the fact that certain diseases are "catching" (at times epidemic), and also that often an attack of some disease may produce immunity to further attacks. Spallanzani (1775) grew bacteria in sterilized media, and discovered anaerobic forms and endospores ("germs") which had a much greater heat resistance than their parent bacteria. Jenner's introduction of vaccination (cowpox, from *vacca*, the Latin for cow), has all but eliminated this disease, which used to wipe out whole populations. Yet as far back as 700 A.D., cow fleas (an insect carrier) were used in China to protect against smallpox.

The modern science of bacteriology grew out of the investigations of a French chemist, Louis Pasteur, who worked on lactic and alcoholic fermentations (1857-1860), the wine and brewing industry (1862-3), and on putrefaction. His work on the diseases of the silk worm (1851-1869) saved the French silk industry. The Franco-Prussian War of 1871 led him from the biospecificity of fermentations to the biospecificity of infections in wounds. From this grew Lister's introduction of antiseptics, and finally to the development of asepsis. Pasteur developed vaccines against anthrax (1877), chicken cholera (1880), swine erysipelas (1882), and finally the successful prevention of the dreaded rabies with attenuated rabies virus.

Pasteur's concept of the specificity of infectious diseases stimulated Robert Koch's development of modern bacteriological technique: isolation and study of bacteria in pure culture in suitable media, and their selective staining by aniline dyes. Villemin (1865) showed that tuberculosis could be inoculated from man to animals and serially in animals; but the causative organism (*Mycobacterium tuberculosis*) was found by Koch only in 1882. A great American authority, when shown this tiny organism in a microscope, exclaimed, "Do you mean to tell me that this tiny thing, which I can hardly see, causes the tremendous damage I find in tuberculosis? It's ridiculous!" And for ten years his mistaken judgment blocked the path to proper treatment and preventive measures.

Soon after the discovery of the diphtheria bacillus (Klebs and Loeffler, 1883-4), Behring (1890) discovered its antitoxin, and soon there was a perpendicular drop in deaths from diphtheria. Introduction by Ramon (1925) of formalin treated diphtheria toxin (toxoid or anatoxin) has, where used, practically eliminated diphtheria in children. Ehrlich's discovery of a "magic bullet", "606" or "Salvarsan", was a great help in syphilis. Later came the sulfa drugs, led mainly by prontosil and sulfanilamide (Domaghi); then penicillin and a host of antibiotics and germicides to prevent, control or cure bacterial and other infections. The protection of water supplies by chlorination and

filtration, and the scrutiny of foods and services, are now accepted routines.

Classification of bacteria is based on a careful study of appearance (morphology), chemical and other growth requirements (temperature, media, trace substances) and behavior (substances and enzymes produced or utilized in the course of growth, and the effects produced in plants, animals or man, often disease). Special staining methods bring out differences not otherwise visible. Textbooks and manuals give what is generally found, but sometimes these labile organisms show marked deviations and variations.

The Gram Stain (Gentian Violet or Crystal Violet, with safranin as a counter-stain) is commonly used as a preliminary test. The methods used to cultivate and identify, e.g., a round bacterium (coccus) or a rod-shaped bacterium (bacillus) are largely determined by whether it is gram-positive (purple) or gram-negative (red). The proper reading of a properly performed Gram stain is, therefore, an important preliminary.

Many bacteria are extremely fastidious and may fail to grow unless the medium on which they are planted contains suitable amounts of the proper peptones, amino acids, sugars, blood, trace substances, etc. They must also have appropriate conditions: pH (acidity or alkalinity), temperature, air supply, etc. Aerobes need air; anaerobes demand absence of air; facultative organisms can grow either in the presence of air or in its absence. Some media are fluid (broths); others are solidified, e.g., with gelatin or agar. Before being inoculated with a bacterial specimen, media are sterilized by heating in an autoclave, usually at 15 pounds steam pressure (giving 121°C.) for 15 to 20 minutes. The Arnold method of fractional sterilization (after Tyndall), consists in heating in free flowing steam at 100°C. for 2 or 3 successive days, allowing the medium to stand at room temperature between treatments. Spores which survive the first or second heating, sprout and are killed by subsequent heating. Egg and sera media, which cannot stand such high temperatures, are treated by inspissation, i.e., heating to 75-85°C. for 1 to 2 hours on 2 or 3 successive days (e.g., Petragani's egg medium or Loeffler serum slants). Media containing extremely sensitive substances (some sugars and sera), are sterilized by ultrafiltration through unglazed porcelain, compressed asbestos or cellulose (Seitz filter), or infusorial earth.

Two types of test plates are used for the isolation of bacteria from mixed cultures or clinical specimens: (1) streak or surface inoculated plates; (2) deep or pour plates, in which the inoculum is added to the melted agar medium before pouring it into sterile Petri dishes. If the inoculum is sufficiently diluted, individual colonies can be "fished out" with a sterile wire loop and replanted on one or more tubes of selected media. The way this isolated organism behaves helps the bacteriologist to determine its classification. Special staining methods are of considerable use here. The final test of a pathogenic organism is what it does to a susceptible plant or animal; thus, a virulent *Mycobacterium tuberculosis* can destroy a guinea-

pig in from two to six weeks. Conditions are important. Pasteur found that chickens whose normal temperature runs about 106–108°F. (40–42°C), resisted virulent anthrax until they were chilled by immersion in ice-water. Furthermore, bacteria and test animals are both variable, and do not always behave in textbook fashion.

Special treatises, e.g., Bergey's "Manual of Determinative Bacteriology", must be consulted for a complete tabular classification of bacteria (Class *Schizomycetes*, Nageli). A mere epitome of the main orders follows.

(1) *True bacteria* (Eubacteriales). Here are included the nitrate and nitrite formers; the autotrophs which can develop on inorganic media; lactic acid bacteria (turn milk sour); sulfur bacteria (oxidize sulfur); colon bacillus (*Escherichia*); typhoid bacillus (*Salmonella*); pneumonia (diplococci). On the basis of agglutination with immune sera (made by injecting dead bacteria into animals), more than 50 serotypes of *Diplococcus pneumoniae* are recognized and about 150 serotypes of *Salmonella*. Others in this huge order are *Staphylococci* (*aureus* produces yellow pus, *albus* produces white pus). *Streptococci* (grow in chains). Real bacteria are supposed to produce no spores, even if rod-shaped. Bacilli (from the Latin *bacillus*, a rod) produce spores. Stalked bacteria (*Caulobacteria*) grow in fresh or sea-water, in sugar vats, etc., and may adhere to solid surfaces by including a sticky "gum". The red, purple, brown or green bacteria (*Rhodobacteria*) can carry on photosynthesis, without liberating oxygen, as do plants.

(2) *Actinomycetales* form elongated cells with definite branching tendency. The *Mycobacteria* (fungus-like bacteria) are polymorphic; besides the classical acid-fast rod forms, they may show coccoidal, amorphous and even motile forms, and also virus-like or submicroscopic forms. They cause such diseases as tuberculosis and leprosy, and have been reported in scleroderma and cancers of both man and animals. *Nocardia* resemble *Mycobacteria* but are even more polymorphic, and show budding, mycelia and spores. The *Streptomyces* have a branching mycelium, and form conidiospores (asexually produced). The best known is *S. griseus*, from which is extracted the antibiotic streptomycin.

(3) *Chlamydo bacteria*, have long sheathed filaments and are algae-like. They include iron and sulfur bacteria.

(4) *Myxobacteria* (slime bacteria), form a swarm (pseudopodium) which can migrate as a unit, in this respect resembling the *Myxomycetes* (slime moulds, which some have regarded as animals).

(5) *Spirochetes* have spiral forms and multiply by transverse fission. *Treponema pallidum* causes syphilis. *Borrelia vincenti* causes ulcerative stomatitis (Vincent's angina), and also pulmonary trouble. *Leptospira*, carried by rats and dogs, causes Weil's disease (spirochetal jaundice).

One effective method of combating bacteria is by introduction into the affected system of a so-called *bacteriophage*—a special type of microorganism that destroys bacteria by penetrating their protective coatings, which are often of a

waxy nature, and literally devouring them. The action is similar to that of a parasite. The white corpuscles (leucocytes) present in the blood also attack and destroy many bacteria. Bacteriophages were discovered by Twort (1915) and d'Herelle (1917).

JEROME ALEXANDER

Cross-references: *Antibodies, Brewing*

BAEKELAND, LEO HENDRIK (1863–1944)

Leo Hendrik Baekeland, son of Karel L. and Rosalia (Merchie) was born in Ghent, Belgium, on November 14, 1863. He was educated in the city elementary schools, the Atheneum, a Government High School. Entering the University at the age of 17 under a Fellowship by the City of Ghent, his success was well on the way when at the age of 21 he received the degree of Doctor of Science, magna cum laude, and after teaching at the Government Higher Normal School in Bruges he returned to the University of Ghent at the age of 26 as Associate Professor of Chemistry and Physics. It was here that he won his first major recognition in competition with other Belgian Scientists. The principal reward was a traveling Fellowship which enabled him to visit Universities in England, Germany, Scotland and the United States.

Of the several countries visited Baekeland preferred the United States and on being offered a position with a photographic firm decided to stay. It was then that he soon felt the difference between academic and industrial life for he said, "confronted with the big responsibility of practical life, my real education began." Almost immediately he commenced experimentation in the photographic field in which he had already attained prestige in Europe. By 1893 a photographic paper was perfected to which he gave the name of "Velox" and established the Nepera Chemical Co., Yonkers, N. Y. This paper utilized a special colloidal chloride of silver relatively insensitive to yellowish and greenish light but more sensitive to blue and violet. Prints could be made independent of weather conditions.

The "daylight paper" was successful and soon Baekeland sold his interests to a large photographic supply house for a liberal sum.

Baekeland next turned his attention to a study of electrolytic processes and after a year of preparation at the electrochemical laboratory of the Technological Institute at Charlottenburg near Berlin, research was begun in his own laboratory in Yonkers, New York. One of the largest and best equipped electrochemical plants in the world resulted from this small beginning.

These commercial successes provided the stimulus to attack new problems, and in 1905 Baekeland started the investigation into the reaction products of phenols and aldehydes. This work proved to be his crowning achievement—the invention of Bakelite phenol-formaldehyde resins. Before the end of 1907 commercial production was commenced in a small way and in 1910 the General Bakelite Company was formed. It is now known as Bakelite Company, a division of Union Carbide and Carbon

Corporation. The basic reaction for the preparation of reaction products of phenols and aldehydes had been known since the early work of Adolph Bayer in 1872, and by others shortly afterwards.

The reaction appeared simple but no one found a way to control it to produce usable resins. Baekeland learned the importance of heat and pressure on this reaction and his earliest patents were based on this understanding. The significance of catalysts was recognized in the control of the reaction. The chemistry of the reaction between phenols and aldehydes has been studied at length since the first announcement by Baekeland in February 1909, until today the literature on this subject is voluminous. The phenol-aldehyde resinous materials became not only significant in themselves, but the discovery of the controlling factors in the polymerizing reaction served to stimulate investigations throughout the entire world. The varieties of synthetic resins are now almost infinite, and the plastics industry touches practically every phase of human activity.

ARCHIE J. WEITH

BANCROFT, WILDER D. (1867-1953)

Wilder D. Bancroft's contributions to the field of chemistry were manifold and during his lifetime he enjoyed wide recognition for his achievements. Before his thirtieth year, he wrote "The Phase Rule" the first exposition in English on this subject, based on Bakhuis Roozeboom's work. One of his greatest services was in founding the *Journal of Physical Chemistry* in 1896. He was its editor for over 35 years and financed it from private resources for some time. From 1913 until his death he was associate editor of the *Journal of the Franklin Institute*. His goal was always to further the study of chemistry, encourage pioneer investigations and broaden the applications of scientific knowledge from one branch of study to another. Dr. Bancroft devoted a great deal of time and energy to the education and direction of students. He was always an inspiring teacher.

Bancroft published papers on plasticity of clay, adsorption of gases, chemotherapy, structural colors, qualities of bread-flour, tapping of trees for turpentine and rubber, drug addiction and the chemistry of anaesthesia. But his prime interest was the chemistry of colloids. His book "Applied Colloid Chemistry" appeared in three editions from 1921 to 1932. During those years he lectured on many varied subjects and in 1928 published "The Methods of Research." This book gives three famous lectures delivered at The Rice Institute. Bancroft also served the National Research Council Committee on the Chemistry of Colloids and the Eighteenth Annual Colloid Symposium in 1941 at Cornell was called the Wilder D. Bancroft Symposium.

Known for his investigations in electrochemistry, Bancroft in 1902 helped found the American Electrochemical Society and was its President twice—in 1905 and again in 1919. In 1910 he was honored with the Presidency of the American

Chemical Society. During World War I, he served his country as Lieutenant Colonel, Chemical Warfare Service where he made his contribution in the dissemination of data on poison gases. His activities included the Vice-Presidency of the International Union of Chemistry (1922-3); the Board of Visitors of the National Bureau of Standards; the Advisory Board of the Cancer Research Fund; and the National Academy of Sciences.

He was elected Honorary Fellow of The Chemical Society, the Polish Chemical Society and the Societe Chimique de France. Lafayette College and the University of Cambridge awarded him the degree of Honorary Doctor of Science (1919; 1923) and the University of Southern California conferred the Honorary Doctor of Laws degree in 1930.

JOHN B. CALKIN

Cross-references: *Colloid Chemistry*

BANTING, SIR FREDERICK GRANT (1891-1941)

Born at Alliston, Ontario, Canada, Banting served overseas as a medical officer in World War I, and then practiced medicine in Canada until 1921. Then, working together with Charles H. Best in the laboratory of J. J. R. MacLeod at the University of Toronto, he began an investigation of the hypothetical internal secretion of the pancreas. At the time, indirect evidence suggested that the isles of Langerhans in the pancreas secrete an anti diabetic hormone, but efforts to obtain an active extract had failed. Banting correctly reasoned that the hormone had been destroyed during these previous extractions by the digestive enzymes also secreted by the pancreas.

On this basis he succeeded in obtaining active anti diabetic extracts by various techniques, such as by using the pancreas of foetal calves which had not yet developed pancreatic digestive enzymes. Then, together with MacLeod and J. P. Collip, he fractionated these crude anti-diabetic extracts to obtain a much purified preparation of insulin, the active principle now used as a specific remedy for diabetes. In 1923 he received the Nobel prize in medicine together with MacLeod, and he was appointed professor of medical research at the University of Toronto. In 1930, the Banting Institute was created in Toronto, and in 1934 Banting was knighted. He lost his life in an airplane accident while in the service of Great Britain during the second World War.

BERNARD JAFFE

BARIUM AND COMPOUNDS

Barium, calcium and strontium are white, and differ among themselves by shades of color or casts. They are malleable, extrudable, and machinable, and may be made into rods, wire, or plate. They are less reactive than sodium and potassium, and have higher melting points and boiling points. Their common ores are the sulfates and carbonates, and they form analogous chlorides, peroxides, nitrates, chlorates, true carbides, and acetylides. The volatilizable salts give in-

acting with chlorine, an acid, to form sodium chloride. The theory is too broad to be generally useful.

It is apparent from the foregoing discussion of several theories that the terms "base" and "acid" are not absolute but relative terms to be used with reference to a particular environment. An amphoteric substance may behave either as an acid or a base depending upon the solvent and reactant. Nevertheless, since many substances are considered to have an intrinsic basicity, an effort will be made to list several common bases and mention their properties and industrial uses.

Alkali Metal Hydroxides. Both NaOH and KOH are white solids which absorb CO_2 and H_2O rapidly from the air, soluble in water, alcohol and ether. Principal uses are in the manufacture of chemicals, rayon and cellulose film, pulp and paper, lye and cleansers, and soaps by saponification of fats, in petroleum refining to neutralize acids, and in reclaiming of rubber to dissolve the fabric.

Alkali Metal Carbonates. Na_2CO_3 and K_2CO_3 and their hydrates are white solids, soluble in water, insoluble in alcohol. Large quantities are used in the manufacture of glass, and other chemicals, chiefly NaOH and NaHCO_3 . Other uses include manufacture of soap, cleansers, pulp and paper, water softeners, and petroleum refining.

Borax and Sodium Phosphates. The chief uses for borax and the sodium phosphates such as their use in cleaning compounds depend primarily on their basicity in aqueous solution.

Quicklime and Hydrated Lime. CaO , a white solid, absorbs H_2O and CO_2 from the air to become air slaked lime. Ca(OH)_2 also absorbs CO_2 from the air. Principal uses are in the building trade for making mortar, agriculture for controlling the acidity of soils, metallurgy for a steel flux and ore concentration, water purification, tanneries for dehairing hides, and manufacture of calcium carbide, cyanamide, and paper.

Ammonia. NH_3 is a colorless gas with a pungent odor, very soluble in water and readily liquefied at moderate temperature and pressure. It is marketed in the anhydrous form or aqueous solution. Important uses are for fertilizers, either by direct addition to the soil or conversion to an ammonium salt by neutralization with H_2SO_4 , H_3PO_4 or HNO_3 , for extracting plant dyes, and for the manufacture of aniline and other amines. It is used in refrigeration because of its physical properties, as an intermediate in the preparation of nitric acid by oxidation, and as a solvent for many chemical reactions. [See further article on Ammonia].

Aliphatic Amines. Methyl-, ethyl-, butyl-, and amylamines, and ethylenediamine are used in manufacturing chemical intermediates, dyestuffs, insecticides, synthetic detergents, corrosion inhibitors, and as solvents. Monoethanolamine is used for absorption of CO_2 from combustion gases. Diethanolamine is used for the absorption of CO_2 and H_2S .

Aniline, 2-Naphthylamine, and Other Aromatic Amines. These are used for manufacture of dyes and intermediates, and synthetic

rubber additives such as diphenylamine and cyclohexylamine.

Pyridine and Its Homologs are used in the manufacture of vitamins, sulfa drugs, and fungicides.

There has been a tremendous increase in interest in reactions in nonaqueous solvents in recent years for use in both synthesis and analysis. Ammonia and derivatives of ammonia, the simple aliphatic amines, ethylenediamine and pyridine are all basic solvents which have been used for reactions for which it was desirable to enhance the acidic properties of the solutes.

W. F. WAGNER

Cross-references: *Acids, pH, Buffers, Blood*

BATING, see LEATHER

BATTELLE MEMORIAL INSTITUTE

Battelle Memorial Institute is an independent, nonprofit organization that provides the plant, equipment, and personnel for basic and applied research on a contract basis. It was established in 1929, at Columbus, Ohio, on the basis of provisions in the will of Gordon Battelle. The last of a family that was prominent in Ohio's iron and steel industry, Gordon left his estate to build and endow an Institute "for the purpose of education . . . the encouragement of research . . . and the making of discoveries and inventions for industry".

The Institute has facilities for research on all types of chemical problems including: (1) theoretical studies; (2) production of chemical materials; (3) investigation of the uses of chemical materials, including by-products; (4) studies of the availability of materials; (5) development of processes and products; (6) pilot plant studies; and (7) manufacturing of finished products.

In addition to research in all general phases of organic, physical, and inorganic chemistry, Battelle carries on investigations in such fields as adhesives, plastics, resins, and rubber; agriculture, including fertilizers, insecticides, fungicides, utilization of by-products, growth inhibitors, etc.; corrosion technology; fuels; organic coatings; electrochemistry; chemistry of solid state materials; application of chemistry to all phases of metallurgy; textiles; petroleum and natural-gas products; coal products; wood preservation and wood technology; chemical aspects of the graphic arts; ceramics; air and stream pollution; radioisotopes and radiation; nuclear research; preservation of foods; and catalysis and surface chemistry.

The Institute also has facilities for studies in chemical structures, thermodynamics, and chemical engineering; surveys of chemical literature; and the investigation of problems relating to the availability, economics, and marketing of chemicals.

In addition to its chemical research, Battelle has 30 divisions at its Columbus laboratories which conduct research in other industrial fields. These divisions cover the areas of ferrous and nonferrous metallurgy, minerals processing and beneficiation, extractive metallurgy, industrial

physics, fuels and combustion, ceramic technology, electrical engineering, electronics, theoretical and applied mechanics, nuclear engineering, welding technology, graphic arts, engineering economics, operations research, agricultural and biological sciences, and information processing.

The Institute's organization is elastic, permitting the formation of research teams composed of technologists from any fields related to a particular investigation. Such teams can attack technical problems from all pertinent angles. Thus at Battelle, chemical aspects of any investigation can be dealt with simultaneously and in conjunction with other aspects.

While Battelle's main laboratories are located at Columbus, Ohio, it also has facilities at Frankfurt/Main, Germany; Geneva, Switzerland; West Jefferson, Ohio; and Daytona Beach, Florida. Institute offices are located in Paris, France; Milan, Italy; London, England; Madrid, Spain; and Washington, D. C. The Institute's main library in Columbus, Ohio, houses 35,000 volumes covering all technical fields. Battelle publishes the *Battelle Technical Review* which includes abstracts relating to all major areas of applied research. Battelle's staff totals 2500 with about 1000 administrative and professional personnel, 600 laboratory personnel, and 900 nonprofessional personnel.

C. E. FEUCHTER

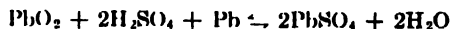
BATTERIES

The work of Volta and others around 1800 on electromotive systems provided the basis for modern electrochemistry, one important subdivision of which is generally known as "battery science". Early investigations were carried out with silver and zinc separated by paper moistened with salt water. The art has developed from that simple system to the point where there are now a number of types of batteries in use throughout the world. These fall into several categories, namely, secondary, primary and energy converters.

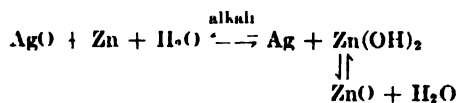
Generally speaking, a battery consists of a positive plate, a negative plate with some separating medium, and an electrolyte (e.g., dilute sulfuric acid) for completing the reaction or acting as a conducting medium. The positive plate is the cathode and the negative plate is the anode, the current being carried by the electrons traveling from the anode to the cathode externally. In solution, the current is carried by ions both positively and negatively charged traveling in opposite directions toward their respective electrodes.

The secondary battery or *storage battery* is one in which the conversion of chemical energy to electrical energy is reversible. In such a system, the electrical energy is stored as chemical energy for whatever period the particular couple is capable of retaining it. Chemical energy is converted to electrical energy by two types of reaction. Certain elements and compounds, when placed in an acid medium, will react with the acid

to yield electrical energy. An example is that of the lead acid battery in which the following formula gives the general reaction:

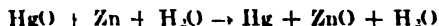
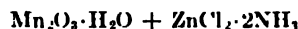
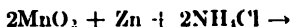


Certain other compounds and elements are capable of furnishing electrical energy when placed in an alkaline medium (e.g., potassium hydroxide). These use the water present in the solution as a carrier for the negative radical in the compound (positive plate) to be transferred to the element (negative plate) thus forming a compound with this element. In this type of reaction the actual alkali does not enter into the over-all reaction. The following equation represents the type of reaction applicable to this:



In each of these types of reaction there is an over-all transfer of two electrons. The main difference between the two types of systems is in the fact that the alkaline systems tend to remain active in the discharge condition for long periods of time and still be capable of storing chemical energy when electrical energy is supplied to it.

In primary batteries the conversion of chemical energy to electrical energy is not reversible. There are several types. One type is manufactured with the elements and electrolyte assembled as a unit. These are usable from the time of manufacture and have a finite span of useful life. These are represented by the Leclanché and the RM or Mercury type *dry cells*. The other type involves the use of a reserve type principle in which the elements are stored in a dry state until the time of use. At this time the electrolyte is added either manually or by automatic means, and the cell is ready for use. Here again the system may be either with an acid or salt solution or an alkaline electrolyte. The Leclanché type represents a salt electrolyte with a strong acid radical, while the Mercury cell represents the alkaline system. The corresponding reactions are given as follows:



In all primary batteries at least one of the elements represents a consumable item which is not replaceable by supplying electrical energy to any successful degree. This lends itself to obtaining a higher output per unit of weight and space than that obtainable from the conventional rechargeable systems.

The next group, which are erroneously called batteries, includes the nuclear and solar energy converters. Here the electrical energy is supplied by a direct conversion either excited automatically, as in the case of the nuclear system, or by an external source as in the solar system. In both of these cases as soon as the exciting source has been removed, no further electrical energy may be obtained. Therefore, they are not truly of the

battery class, since electrical energy cannot be stored directly. Various expedients are used, such as charging condensers or storage batteries to overcome this deficiency.

In the case of nuclear energy converters there are two different approaches. In one case the electrical energy is collected from the Beta ray emission which gives a very low order of magnitude of current; however, the voltage may build up to several thousand volts from a single source. In the other case the principle involves surface emission of electrons due to a Beta ionizing environment. In this case the voltage is fixed at approximately 1.5 to 3 volts and the current is proportionate to the intensity of the ionization. Several versions of these two principles have been investigated by various organizations using different materials. In all cases use is limited to use in extremely low order of magnitude current applications.

Solar energy converters basically operate on the same principle as that of the photo-electric cell. However, due to improved junctions and purer materials, it is possible to realize a higher magnitude of electrical energy. Normal solar bi-valves will give .4 volts at approximately .25 A. per sq. in. If higher currents are demanded the voltage drops off sharply. Therefore, in order to make a practical unit it is necessary to have large surface areas and a multiplicity of units to give the proper voltage and current combinations. More sensitive materials are now being investigated which are actuated by the use of the ordinary electric light rather than by the sun's rays.

The rate of a chemical reaction is based on reaction velocities, concentration and temperature. Generally speaking, these same factors apply in the case of batteries since in all true battery systems there is a chemical change which takes place when electrical energy is furnished. The first two items have been compensated for in the overall development of the presently available batteries. The effect of temperature has not been compensated for. As shown in the actual rate of reaction formula for the various orders of magnitude, the effective temperature is an important factor. As the temperature is lowered, the rate of reaction is decidedly reduced. This shows up in the actual battery by a reduction in maximum current available at a usable voltage. Likewise, when the temperature rises, the rate of reaction increases rapidly. This also induces side reactions in the basic reaction which, in the case of the battery, shows up as local action. Here the voltage and current gain are large in comparison to that at the low temperature.

A battery may consist of one cell or a multiplicity of cells which will have a voltage of the couple alone or a multiple of this couple. The volume and weight required to furnish a definite amount of electrical energy is dependent upon the chemical equivalent of the particular materials used in the battery. Generally these are arrived at by the formula:

$$\frac{\text{Atomic mass}}{\text{Valence}} = \text{Chemical equivalent}$$

This is further reduced to gm/AH by dividing the chemical equivalent by 26.8. This gives the theoretical amount of energy available. The actual amount of useful energy available may be much less than this theoretical value, i.e., lead has 3.84 gm/AH theoretical and 8 gm/AH actual. The rating of batteries is usually based on a WH per pound or WH per cubic inch basis and depending upon the couple used this will range from 10 WH per pound to 60 WH per pound and from .5 WH per cubic inch to 8 WH per cubic inch. Batteries to date are still the main source of DC power reliable for service.

The following types of batteries are now being produced:

Secondary Batteries: Lead Acid; Nickel Iron alkaline (Edison); Nickel Cadmium alkaline; Silver-Zinc alkaline

Primary Batteries (Standard): Leclanché dry cell using either Zinc, Magnesium or Aluminum as the negative; RM or Mercury cell

Primary Batteries (Reserve): Lead dioxide Zinc or Cadmium-Sulfuric Acid; Lead dioxide Lead Perochloric or Fluoboric acid; Silver chloride-Magnesium water activated; Cuprous chloride Magnesium water activated; Silver dioxide-Zinc alkaline

P. L. HOWARD

Storage Batteries

Lead Batteries. The lead battery requires a large number of thin plates (from 12 to 17) to supply the heavy currents required for automobile cranking. Other lead batteries are made with fewer and thicker plates where heavy currents are not required but a longer life is desired. The manufacturing process usually begins with the casting of a framework or grid. A paste consisting principally of lead oxide is applied to this grid and dried. The plates are then charged, assembled and put into a container. The grid is a lattice work which supports the active material and conducts electric current to the battery terminals. These grids are usually cast from antimonial lead (lead containing 7% to 12% antimony, and smaller amounts of tin, copper and arsenic).

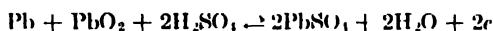
The paste has in the past been made from a wide variety of lead compounds. Most paste is made by mixing a litharge containing 20 to 30% metallic lead with dilute sulfuric acid to give a paste of the desired density and consistency. The paste is then applied to the grids in automatic machinery and passed through an oven which partly dries the plates. Finally, the plates are allowed to stand or cure for several days while the residual moisture dries, and most of the metallic lead is oxidized. This gives plates of good mechanical strength without introducing foreign "bonding agents" or requiring precisely controlled drying conditions.

The oxide used for the negative plates contains about 1% of materials called *expanders*. These comprise carbon black, barium sulfate and an organic material usually derived from the lignin fraction of wood. They prevent a deterioration of plate capacity and a shrinking of the sponge lead.

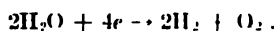
and also improve the capacity during a high rate low temperature discharge.

After the plates have been cured, they are assembled and given their first charge. This charge is usually carried out in dilute sulfuric acid at a specific gravity of about 1.100, since a higher strength acid retards charge. After this first, or forming charge, the acid is replaced by a stronger acid. Maximum initial capacity for cold weather operation is attained with 1.300 acid. For high-temperature operation, a much better life is attained with 1.220 acid. Most batteries are made with 1.250 to 1.275 acid. This is measured at 80°F compared with water at 60°F. The charge process converts the negative plate to sponge lead and the positive plate to lead dioxide.

The ordinary automobile battery weighs about 40 pounds, contains 3 cells, will deliver about 6 volts, and has a capacity of 100 ampere hours at the 20 hour rate. It will deliver 300 amperes for about 3.5 minutes at 0°F and an initial voltage of about 4.3 volts. It is kept fully charged by a generator which may deliver as much as 40 amperes to a discharged battery. The amount of charge current is controlled by a voltage regulator. Whenever the battery voltage rises to about 7.5 volts, the charge current is automatically reduced to avoid excessive overcharging. The chemical reaction normally occurring in a battery is:



when e is 96,500 ampere seconds if molecular weights are in grams. This reaction proceeds in either direction readily without the development of much heat, and without the consumption of water or production of gas. When a battery is given an overcharge, water is decomposed by the reaction



This reaction produces considerable heat, consumes water, and because of the high voltage and heat, tends to shorten battery life. With a good voltage regulator, water consumption of a battery is small and water is added to the battery not more than four times per year. Excessive water consumption, or zero water consumption, indicate something wrong with the electrical system of the automobile. The water added to the battery is usually specified as distilled water, but almost any water that is safe to drink is also harmless to the battery.

The life of a battery depends on the service it receives. It is customary to guarantee a battery for 18 months or 18,000 miles, whichever occurs first. The average battery in private automobile service will last 24 to 36 months. The most frequent cause of failure is corrosion of the positive grid. No method of extending this life without sacrifice of other important properties has been proved by laboratory and field test.

Industrial lead batteries are designed for a longer life. To attain this, they are made heavier and sacrifice high rate performance. They are somewhat more expensive than automobile batteries, but have a life of five to thirty years.

Where industrial type batteries are discharged and recharged frequently, there is a tendency of the positive active material to disintegrate and fall to the bottom of the cell. This can be retarded by the use of a barrier such as a glass mat or a perforated rubber envelope, or a combination of the two against the surface of the positive plate.

Where batteries are used for stand-by service, the self-discharge is important. That is, when a battery is not being used and is left without either charge or discharge, there is a gradual loss of capacity. This amounts to 0.5 to 1% per day with automobile batteries at 80°F, and somewhat lower values for industrial batteries. Where batteries are used in stand-by service, they are usually given a low rate charge just sufficient to make up for this self-discharge. This is called a floating charge and normally is voltage controlled at 2.15 to 2.20 volts per cell.

Nickel-Iron Batteries. Between 1900 and 1910, Thomas A. Edison developed a nickel-iron battery which has found extensive use. It is mechanically more rugged than the lead battery. It uses an alkaline electrolyte which is less corrosive, and its active materials withstand electrical abuse in the form of overcharge, incomplete charging or prolonged idle periods. It also withstands high temperatures better and in general has a much better life. Its higher cost and different electrical characteristics have limited its use to electric truck propulsion and related heavy duty services. In general, it is not used where exceptionally heavy currents are required, such as for automobile cranking, or where low temperature operation is required.

The chemistry of the nickel-iron battery is not fully worked out. The reaction has been written: $\text{Fe} + \text{NiO}_2 + 4\text{H}_2\text{O} \rightarrow \text{Ni} + \text{Fe(OH)}_2$

The voltage obtained indicate that probably two different higher oxides of nickel are present and are mutually soluble. Other studies indicate that the nickel oxides are hydrated. The electrolyte is potassium hydroxide containing lithium hydroxide, and the specific gravity is 1.21.

The negative plates are prepared from iron oxide containing a small amount of mercury oxide. These are surrounded by a nickel plated steel pocket pierced by many small holes to allow electrolyte and current to reach the active material. The positive plate consists of tubes of nickel plated steel with reinforcing bands. The active material is nickel oxide with alternate layers of metallic nickel flake to supply electrical conductivity.

The cell delivers an average of 1.25 volts during discharge at the five hour rate. Consequently, it requires approximately five cells to do the work of three lead-acid cells. The cells, however, are smaller, and lighter so that the overall battery weight is slightly less and the volume somewhat higher than a lead battery of the same power output. The battery is usually rated at the 5 hour discharge rate, that is a 500 ampere hour battery will deliver 100 amperes for 5 hours. The normal charge is 100 amperes for 7 hours with this battery. This overcharge makes it necessary to ventilate

the battery compartment sufficiently to carry off the heat developed, as well as the hydrogen and oxygen.

Nickel-Cadmium Batteries. If cadmium is substituted for the iron of the negative plate of the nickel-iron battery, it becomes possible to float charge the battery, and also to discharge it at low temperatures. The result is the "tubular" type nickel cadmium battery. Only the positive plates are of tubular construction. This difference in negative active material gives a battery which has achieved considerable success in Europe.

If the tubular positives of such a battery are replaced by pocket type positives, the battery has a better high rate performance, but a somewhat inferior cycle life. The pocket type positive contains nickel oxide but uses graphite for electrical conductivity instead of the nickel flake used in tubular positives. These pocket type nickel cadmium batteries are manufactured in various plate thicknesses depending on the service desired. Thin plate batteries have a good high rate performance, but sacrifice low rate performance and are quite bulky.

A third type of nickel cadmium battery uses sintered plates. For these batteries a special grade of nickel powder is heated in a mold until the particles just begin to adhere. The pores of these plates are then impregnated with a solution of the nickel nitrate to make positive plates and with cadmium nitrate to make negative plates. If these plates are made quite thin, a battery is obtained which has excellent high rate performance, even at low temperatures.

These various types of nickel cadmium batteries have not yet attained wide acceptance in the United States. They are relatively expensive and except for the sintered plate battery considerably more bulky than other batteries. They have a major advantage because their shelf life is excellent. Under best conditions, a battery will retain 50% of its initial capacity after a year of idleness. Another advantage is that they can be easily charged at low temperatures.

Silver-Zinc Batteries. A still more recent development is the silver zinc battery. This is an extremely expensive battery of relatively short life, but with a tremendous power output during a high rate discharge. The chemical reaction is: $\text{Ag}_2\text{O} + \text{Zn} \rightarrow \text{ZnO} + \text{Ag}$.

The discharge voltage is 1.4 to 1.3 volts. The positive plate is a porous silver peroxide sponge, usually with a support of metallic silver. The negative plate is spongy zinc.

This couple has been known for many years, but it was not a successful storage battery because zinc oxide is soluble in the potassium hydroxide electrode. The discharge product would, therefore, settle to the bottom of the cell and during charge form spongy zinc not available for further useful work. Also a part of the silver would go into suspension and contaminate the zinc plate with metallic silver, where it promoted rapid self discharge. The development of a separator which would prevent the migration of silver and zinc was needed to make the battery useful. Such separa-

tion has been developed, and the silver-zinc battery is now a commercial article.

I. W. WILLIHNANZ

Cross-references: *Electrochemistry, Ions*

BEILSTEIN, FRIEDERICH KONRAD (1838-1906)

A noted German chemist who almost single-handedly compiled the first two editions and the main part of the third edition of his renowned "Handbuch der Organischen Chemie". He was born February 17, 1838 in Petrograd of German parents. After early education in the German schools of Petrograd, he studied under Bunsen at Heidelberg, Liebig at Munich, and with Wöhler at Göttingen where he received his doctor's degree in 1857. Following study with Wurtz in Paris and a brief assistantship with Lowig at Breslau, he returned as privat dozent at Göttingen for six years, 1860-66. Beilstein was invited to succeed Mendeléeff at the Imperial Technological Institute at Petrograd where he remained until his retirement.

After election to the Russian Academy of Science in 1887, he received a sufficient stipend to cease his teaching and devote himself to his handbook. The first edition was sent in almost complete form to the publisher who accepted and published it within two years 1880-82. With the aid of a single assistant, the second edition was compiled and published from 1886-90. When the growth of organic chemistry indicated too colossal an undertaking for one individual, Professor Paul Jacobsen was invited to be co editor of the third edition. As Professor Jacobsen declined, the suggestion was made and carried out that the work be continued under the auspices of the German Chemical Society. Jacobsen became the editor of the supplement of the third edition which was published two weeks before Beilstein died on October 18, 1906. At once plans were made for the fourth edition so that Beilstein's name will always be a byword in chemical circles.

Beilstein also published about 100 papers on experimental research. Topics include the effect of temperature upon chlorination of organic compounds, a halogen test, isomerism of nitrotoluenes, and the composition of petroleum. With Fittig and Hubner, he was editor of "Die Zeitschrift für Chemie," from 1865 to 1871.

VIRGINIA BARTOW

BERYLLIUM AND COMPOUNDS

Beryllium Metal. The element beryllium has an atomic number of 4, an atomic weight of 9.013 and is in Group II of the Periodic Table. It has a single valence state of +2, corresponding to 2s electrons in the L-shell. It has only one stable isotope. The steel-gray metal, of close-packed hexagonal crystal structure, is the only stable light metal (sp. gr. = 1.847) with a high melting point (1,285°C.). It is estimated that beryllium occurs in the earth's crust in the amount of approximately 0.0005%. Thus, it is somewhat more abun-

dant than arsenic, but less abundant than cesium. Beryl ($3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) is the only mineral of beryllium that is of commercial importance. The present largest sources are South America (Brazil, Argentina), Southern Africa, Southern Rhodesia, India and French Morocco.

The production processes now in use involve three general steps: (1) production of beryllium hydroxide or oxide from beryl ore by either the Copaux-Kaweecku Process (Beryllium Corp.) or the Sawyer-Kjellgran Process (Brush Beryllium Co.); (2) conversion to beryllium chloride or fluoride and (3) reduction to beryllium metal.

Many of beryllium's chemical properties are intermediate between those of magnesium and aluminum. All the common mineral acids attack beryllium metal readily with the exception of nitric acid, which if cold and concentrated, is without effect. Alkalies react with beryllium with the evolution of hydrogen to first form beryllium hydroxide. Excess alkali will convert the hydroxide to a water soluble beryllate (such as Na_2BeO_4). This differs from a similarly formed aluminate in that the beryllate is fairly easily hydrolyzed by heating or diluting its solution.

At ordinary temperatures in normal atmosphere, beryllium metal shows good resistance to oxidation. At temperatures above 700°C , oxidation becomes noticeable, increasing progressively with increase in temperature. Above 900°C , nitrogen attacks beryllium forming beryllium nitride (Be_3N_2); and carbon combines with beryllium to produce beryllium carbide (BeC).

Owing to its low atomic weight, beryllium has an x ray transmission factor 17 times greater than aluminum and 6-10 times greater than Lindemann glass. This property, combined with its good strength and high melting point makes it ideally suited for windows in x ray tubes, especially where longer wave x rays are desirable. It has proved advantageous in x ray diffraction work and microradiography.

Beryllium has an electrical and thermal conductivity approximately 40% of that of copper, a thermal expansion about the same as steel and a sound transmission $2\frac{1}{2}$ times greater than steel. It is as light as most magnesium alloys while it has a strength-weight ratio superior to titanium or aluminum alloys.

Despite its many interesting properties, beryllium, so far, has had only limited commercial application, discounting its principal use as a hardening agent in alloys. It is invaluable as a shielding and control agent in nuclear reactors, as its low neutron-capture and high neutron-scattering cross sections make it a good moderator and/or reflector of neutrons.

Beryllium Alloys. Beryllium-aluminum base alloys have so far been used only in moderate quantities because of difficulties in producing large sound castings. However, since small additions of beryllium to aluminum impart high strength, thermal stability and unusual oxidation resistance, potential uses may develop. A 25% beryllium alloy has a present limited application in camera shutters.

Because of their unique properties, beryllium-

copper alloys have many applications in industry and are of great commercial and strategic importance. They have excellent formability before heat treatment and remarkable increase in strength and hardness after a simple low-temperature precipitation-hardening. They exhibit structural properties comparable to those of alloy steels. Among their many uses may be listed engine parts subject to extreme wear, vibration, or shock loading; high strength, current-carrying springs; precision-instrument diaphragms, bellows, springs and bourdon tubes; heavy duty brake and clutch drums; molds; and safety tools.

Beryllium-iron alloys exhibit heat-hardening effects, but are coarse-grained. This, however, can be partially counteracted by addition of nickel. Addition of 1-2% beryllium to stainless steels increases strength and hardness, particularly at elevated temperatures, and improves corrosion and impact resistance.

Beryllium-magnesium alloys are difficult to prepare because magnesium has a boiling point (1120°C) lower than the melting point of beryllium (1285°C) and because of little mutual solubility or compound formation. However, addition of very small quantities of beryllium (0.05-0.1%) to magnesium greatly reduce the flammability of magnesium and retards its oxidation at the melting point.

Beryllium nickel base alloy containing 1.7 to 2.1% beryllium is heat hardenable in much the same manner as high beryllium copper. Its outstanding attribute lies in its ability to be work-hardened. Potential applications for diamond drill bit matrix metal, watch balance wheels and springs, hypodermic needles and surgical instruments are indicated.

Compounds of Beryllium. *Basic beryllium acetate* [$(\text{Be}_4\text{O}(\text{C}^+\text{H}_3\text{O}_2)_6$, m.w. = 406.35, sp. gr. = 1.36) is soluble in hot glacial acetic acid and can readily be crystallized therefrom in very pure form. It is also soluble in chloroform and other organic solvents and melts at about 330°C without decomposition. It is used as a source of pure beryllium salts.

Beryllium carbide (BeC , m.w. = 30.036, sp. gr. = 1.91) is produced when beryllium metal powder, intimately mixed with sugar carbon is heated, in the absence of air, to temperatures of 900°C greater. The finely hexagonal, crystalline beryllium carbide is hard and refractory. It is attacked vigorously by strong, hot alkali solutions forming methane gas and alkali-beryllate. It has found limited use in atomic energy applications.

Beryllium chloride (BeCl_2 , m.p. = 440°C , b.p. = 520°C , sp. gr. = 1.599) is a highly deliquescent, crystalline compound. It dissolves in water with great avidity accompanied by hydrolysis evolving hydrogen chloride. It is soluble in ether and alcohol. Its vapor pressure is already high at its melting point.

Beryllium fluoride (BeF_2 , m.w. = 47.01, m.p. 800°C , sp. gr. = 1.986²⁵) is used in the production of beryllium metal by reduction with magnesium metal. Finely ground BeF_2 is readily soluble in water and in alcohol. It is produced by the thermal

decomposition (at 900–950°C) of ammonium beryllium fluoride.

Beryllium hydroxide $[\text{Be}(\text{OH})_2]$ is known to exist in two forms. The "Alpha" hydroxide is a chemical individual of definite composition. It is a granular, crypto-crystalline powder prepared by precipitation from strongly alkaline solution of beryllate and drying at 100°C to $\text{BeO} \cdot 11\text{H}_2\text{O}$. The "Beta" hydroxide is gelatinous and of indefinite composition. In either form beryllium hydroxide begins to decompose to beryllium oxide at 190°C, its transformation being complete at red heat.

Beryllium nitrate $[\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$, m.w. = 187.08, m.p. 60°C is produced commercially by dissolving beryllium oxide or hydroxide in concentrated nitric acid and crystallizing out the nitrate salt. The crystals are deliquescent and have a strong odor of nitrogen pentoxide. It is fairly unstable and decomposes completely into beryllium oxide and nitrous gases at low red heat, suiting it for introducing beryllia into incandescent mantles.

Beryllium nitride (Be_3N_2) is produced by heating beryllium metal powder in a dry, oxygen-free nitrogen atmosphere at temperatures of 700–1400°C. The hard, refractory nitride reacts with mineral acids to form the corresponding salts of beryllium and ammonia. Strong alkali solutions attack it readily, liberating ammonia. It has applications in the nuclear energy program and is currently used in producing the radioactive carbon isotope (C^{14}) for tracer uses.

Beryllium oxide (BeO), m.w. = 25.013, m.p. = 2570°C, sp. gr. = 3.025, sp. heat = 0.209 cal/g at 100°C and Mohs hardness = 9) is a white, high temperature refractory. It is characterized by its excellent thermal conductivity, high electrical resistance even at elevated temperatures and good resistance to thermal shock and to chemical attack. These important properties coupled with good strength suit it admirably for refractory crucible material. In addition, it has high dielectric strength. It has found use as a neutron reflector in power reactors. Other uses include liners for rocket and combustion chambers and high temperature electric furnaces, additive in special glass for high-speed light transmission and component in phosphors for television screens and x-ray equipment.

Beryllium sulfate ($\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, m.w. = 177.14, sp. gr. = 1.713) is readily water-soluble, of definite composition, stable and well adapted to crystallization (a saturated water solution contains 30.5% BeSO_4 by weight at 30°C and 65.2% BeSO_4 at 111°C). When heated in air it progressively loses water of crystallization, resulting in the anhydrous salt at 400°C. This is stable up to 530°C; at 550–600°C, sulfur trioxide is slowly lost and at 1000°C the conversion to beryllium oxide is complete.

Toxicity. During recent years medical research groups have devoted much time to the study of the effect of beryllium and its compounds on the human body. The exact role played by the beryllium atom itself is not clearly understood, especially since the intensity of the attack on the skin or mucous membranes varies greatly with the

element or the elements combined with the beryllium atom and with the individual exposed. As far as is known, no cases of digestive poisoning due to ingestion of beryllium have been recorded in the beryllium industry, and further, no cases of dermatitis or pneumonitis have been reported as due to the mining of beryl ore, or the mechanical working or handling of low beryllium alloys, such as the beryllium copper alloys now in use. However, soluble compounds of beryllium may cause dermatitis, and acute pneumonitis may be encountered when mists, dust, or fumes of these compounds from melting the metal and its alloys, are inhaled. The sensitivity of individuals varies greatly. A few individuals are supersensitive and therefore cannot be employed in the beryllium industry. Medical authorities assert also that mists, dust, or fumes containing beryllium or its compounds may be instrumental in causing a delayed type of pneumonitis, which develops relatively slowly and may extend over a period of years. This health hazard is less understood than dermatitis and acute pneumonitis, and has been the subject of extended investigation by the United States health authorities and other medical groups to determine any participation of beryllium or its compounds in the development of this disease.

The beryllium health hazard is effectively reduced by proper ventilation, frequent washing of the hands, arms, face, and neck, and showers at the end of each shift. It is also advisable to have the plant physician check the chest of every employee at frequent intervals and to x ray all employees at least once a year.

BENGT KJELLGREN AND F. A. VINCI

BERZELIUS, JONS JAKOB (1779–1848)

A noted Swedish chemist, chief arbiter of the chemical world for many years. He was born August 20, 1779 at Vänersunda, Östergötland, Sweden. After his early years at the Linköping Gymnasium and the University of Upsala, where he studied medicine, he held several positions before he was professor at the Karolinska Institute in Stockholm.

His contributions to chemical theory and practice were fundamental. To substantiate Dalton's Atomic Theory, Berzelius determined atomic weights for 43 elements. The accuracy of his results established quantitative analysis as the criterion by which all subsequent theories must be proved. Berzelius proposed his dualistic theory by which unions of positive and negative substances with recognized individual entities, elementary or compound, produced all compounds. This theory emphasized oxides and the association of electricity with chemical affinity. The dualistic theory was overthrown by its inapplicability to ammonia, hydrogen halides, ternary compounds, and organic molecular structure.

Berzelius recognized and coined the words for isomers and catalysis. To him we owe our modern symbols with their quantitative significance, an early classification of minerals by their chemical

composition, perfection of blowpipe analysis, clear recognition of organic radicals which maintain their identity in a series of reactions, and a number of theories about organic molecular structure. He discovered selenium and thorium, and isolated silicon, titanium, and zirconium.

Berzelius was the author of a textbook for chemistry and from 1819 to his death prepared an annual survey of chemistry, his well known "Jahresbericht". He taught many famous men, C. G. Gmelin, Mitscherlich, both Heinrich and Gustav Rose, and Wohler. After many honors including that of baron, Berzelius died August 7, 1848.

VIRGINIA BARTOW

BET THEORY

The data of adsorption can be most conveniently represented by adsorption isotherms, i.e., plots of the amount of material adsorbed against its partial pressure, concentration or activity after equilibrium is established in the system at a constant temperature. In the literature of the adsorption of gases and vapors, five different types of isotherms have been found, as shown in Fig. 1. A complete theory of these isotherms would furnish a complete understanding of the phenomenon; however, such theory does not exist. The BET theory offers a qualitative explanation for all five isotherm types but only a partial solution of the quantitative aspects of the problem.

The first theoretical treatment of the adsorption isotherm was advanced by Langmuir in 1915. He reasoned that at equilibrium the amount adsorbed on a given adsorbent was constant at a given temperature and pressure; consequently, the rate of adsorption must be equal to the rate of desorption. He assumed that (a) adsorption took place only on the bare surface of the adsorbent, i.e., only a single layer was adsorbed; and (b) the rate of desorption was directly proportional to the amount adsorbed. The second assumption implies a constant heat of adsorption throughout the entire range of adsorption.

On the basis of these two assumptions Langmuir derived the equation

$$\theta = \frac{v}{v_m} = \frac{b p}{1 + b p} \quad (1)$$

where θ is the fraction of the surface covered with adsorbed molecules, v is the volume of gas adsorbed, v_m is the volume of gas necessary to cover the entire surface with a unimolecular layer of adsorbed gas, p is the equilibrium pressure, and b is a constant at constant temperature. Eq. (1) gives a good representation of the Type I isotherm, shown in Fig. 1.

The adsorption of vapors in most cases gives Type II, or S-shaped, isotherms. In 1938 Brunauer, Emmett and Teller published an equation that accounted for this type of isotherm. They discarded the idea that vapor adsorption was unimolecular, and used, instead the following assumptions: (a) adsorption was multimolecular,

and each separate layer obeyed a Langmuir equation; (b) the average heat of adsorption in the second adsorbed layer was the same as in the third and higher layers, and it was equal to the heat of condensation of the vapor; and (c) the average heat of adsorption in the first adsorbed layer was different from that of the second and higher layers. The equation, in its linear form, is

$$\frac{p}{v(p_s - p)} = \frac{1}{v_m c} + \frac{(c - 1)}{v_m c} \frac{p}{p_s} \quad (2)$$

where p , v and v_m have the same meaning as in Eq. (1), p_s is the saturation pressure of the vapor (or the vapor pressure), and c is a constant at constant temperature. Harkins named Eq. (2) the BET equation, from the initials of its authors.

Most vapor adsorption isotherms plotted according to Eq. (2) give straight lines in the range $p/p_s = 0.05$ to 0.35. The constants v_m and c can be calculated from the slope and intercept of the straight line. From v_m the surface area of the adsorbent can be evaluated. The number of molecules that cover the adsorbent with a complete monolayer is given by v_m , and the area covered by a molecule is obtained (a) by calculating a spherical volume for the molecule from the density of the liquid, and (b) by assuming hexagonal close-packing of spheres on the surface. An alternative method of obtaining the area of a molecule is to use a two dimensional analog of the van der Waals equation. The two methods give approximately the same molecular surface areas.

The surface area values obtained for a variety of adsorbents by means of the BET equation agreed in all cases within a few per cent with the surface areas determined by direct visual means (e.g., by electron microscope), where such determinations were possible. For porous adsorbents a number of indirect surface area measurements confirmed the BET values. Thus, at present, the method is regarded as the most reliable one for the determination of the surface areas of finely divided substances, and largely because of this the BET equation is the most widely used isotherm equation in the field of adsorption.

The constant c is given by

$$c = c_1 e^{(E_1 - E_L)/RT} \quad (3)$$

where c_1 is another constant, E_1 is the average heat

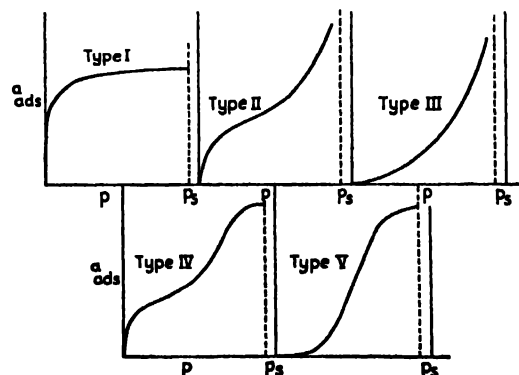


Fig. 1. Types of physical adsorption isotherms.

of adsorption in the first layer, E_L is the heat of liquefaction of the vapor, R is the gas constant and T is the absolute temperature. The difference $E_1 - E_L$ is called the net heat of adsorption. Cassie and Hill independently derived an equation, formally identical with the BET equation, by statistical mechanics and found that

$$c_1 = j_a/j_s \quad (4)$$

where j_a and j_s are the pressure-independent parts of the partition functions of the adsorbate and the liquid, respectively.

From the constant c one can obtain an approximate estimate of E_1 , the average heat of adsorption in the first layer, and the values so obtained are in semi-quantitative agreement with the experimental results. Eq. (2) also correctly describes the temperature dependence of the adsorption isotherms.

The equation gives too low adsorption values below $p/p_s = 0.05$ and too high values above $p/p_s = 0.35$. The former discrepancy is caused by the heterogeneity of the surface of the adsorbent, the latter by the pore structure of the adsorbent.

The BET equation was derived for adsorption on a free surface, and it was assumed that at p_s an infinite number of layers could build up on the surface of the adsorbent. In a porous adsorbent even at saturation pressure only a finite number of adsorbed layers can build up. For this case the isotherm equation is

$$\frac{r}{r_m} = \frac{cx}{1-x} \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (c-1)x - cx^{n+1}} \quad (5)$$

where x is the relative pressure (p/p_s), n is the maximum number of layers that can be adsorbed, and the other terms have the same meaning as in Eq. (2). For $n = \infty$, Eq. (5) reduces to Eq. (2), and for $n = 1$ it reduces to the Langmuir equation, Eq. (1).

The three-parameter BET equation gives a better fit at higher relative pressures than the two-parameter equation, but it does not fit the data up to saturation pressure. Pickett, Anderson, Cook, Dole, Huttig and others introduced semi empirical modifications of the BET equation and obtained better fits at higher relative pressures for certain isotherms. There exists, however, no isotherm equation that can give good agreement with experiment throughout the entire pressure range, from $p = 0$ to $p = p_s$.

The theoretical interpretation of the Type III IV and V isotherms of Fig. 1 was given by Brunauer, Deming, Deming and Teller. They showed that Eq. (2) represents a Type III isotherm if $c = 1$ or smaller. The data of Reyerson and Cameron for the adsorption of bromine and iodine on silica gel were well fitted by the equation. Also, the surface area of the adsorbent, the average heat of adsorption and the temperature dependence of the isotherms were accurately given by the equation.

In the Type IV and V isotherms the attainment of saturation adsorption below saturation pressure was attributed to capillary condensation. A four-parameter equation was developed, in which the fourth parameter was dependent on the heat of

capillary condensation. The equations fitted certain experimental data fairly well; the surface area and the temperature dependence were accurately obtained, and reasonable values were found for the heat of adsorption and the heat of capillary condensation.

STEPHEN BRUNAUER

Cross-references: Adsorption

BILE ACIDS

The bile acids are monocarboxylic acids of the steroid group with 21 atoms and one to three secondary hydroxyl groups. They occur in the bile of all vertebrates from the teleosts upward, mostly in peptidic conjugation with glycine or taurine. The hydroxy groups are situated on C₃, C₆, C₇, and C₁₂, all in α -position (see table).

The bile acids are the most important ingredient of the bile, the secretion of the liver, which is stored in most vertebrates in a gallbladder; there the bile is concentrated and its reaction changes from slightly alkaline to weakly acidic. Hence it is intermittently released into the duodenum where it emulsifies the alimentary lipides prior to their hydrolysis by pancreatic lipase. About 90% of the total amount of bile acids excreted is re-absorbed further down in the intestine. Thus, the liver has to replace only the portion lost with the feces and through catabolism. Oxidation of the bile acids leads as a first step to the conversion of the secondary hydroxy groups to keto groups. Some such keto acids have been isolated from animal bile. The *in vitro* oxidation product of cholic acid, dehydrocholic acid (3,7,12-triketocholanic acid) is used as a choleretic, i.e., as a stimulant of the bile flow.

Name	α Hydroxy Groups in Positions
Lithocholic acid	3
Hydrodeoxycholic acid	3 6
Chenodeoxycholic acid	3 7
Dihydroisobuthocholanic acid	3 12
Iso deoxycholic acid (synth.)	3 21
Cholic acid	3 7 12
β Phocacholic acid	3 7 23

Bile acids share with fatty acids the power to hemolyze red blood corpuscles. More specific is their ability to induce the lysis of live pneumococci, the so called Neufeld phenomenon, which is widely utilized in bacteriological technique. Dehydrogenation of a bile acid derivative leads to the pentacyclic aromatic methyleholanthrene, one of the most potent chemical carcinogens. A number of naturally occurring steroids also shows minor carcinogenic activity. However, the hypothesis that aromatization of steroids takes place in the animal body and leads to actual carcinogenesis has been discarded.

Various color reactions are specific for bile acids; they go back to Pettenkofer's reaction with sucrose and concentrated sulfuric acid; in numerous modifications the sugar has been replaced by furfural, vanillin and other compounds, and concentrated sulfuric acid by more dilute sulfuric acid, phosphoric acid and hydrochloric acid. The

ultraviolet absorption before and after treatment with sulfuric acid (65%) seems to give the best differentiation of the two most important bile acids, cholic acid and desoxycholic acid.

Toxoids, which show peculiarities in steroid metabolism in connection with the elaboration of their poisonous secretion, also contain unusual bile acids with 27 carbon atoms. While the teleost fish produce bile acids, the elasmobranchs use in lieu of bile acids the sulfate ester of a neutral steroid, seymnol ($C_{27}H_{46}O_6$), a tetravalent alcohol with an oxide bridge. Related neutral polyhydroxysteroids, presumably intermediate in the formation of bile acids, have been found in cod's bile, when synthetic processes are slowed down during "hibernation".

The steroids in general and the bile acids in particular exhibit a great tendency to form complexes with fatty acids, hydrocarbons, and other organic compounds. This property is most pronounced in desoxycholic acid; the resulting coordination compounds are known as "choleic acids". They show the usual coordination numbers 1, 2, 4, 6 and 8 molecules of desoxycholic acid to one molecule of the "cholic" component. They exist in the crystalline state and their composition is revealed by melting point diagrams. They dissociate in solution. Whether they are built on a central or axial symmetrical plan, has not yet been decided by x-ray crystallography. Because of the optical activity of desoxycholic acid, choleic acids may serve to resolve racemates.

HARRY SOBOTKA

Cross-references: *Steroids; Hormones (Steroid)*

BINDING AGENTS (RESINOUS)

Some resinous materials, both natural and synthetic, have an affinity for wetting other surfaces. When these liquid resinous substances are thickened, either by evaporation of volatile matter or because of inter- or intramolecular chemical reactions, the tendency to adhere to other surfaces may be preserved. This capacity of a low viscosity resin to wet a surface and to retain adhesiveness after thickening is the chief property of binding agents. This feature is utilized in the compounding of adhesives, paints and plastics.

Despite many years of intensive research, relatively little is known about why some types of resins, such as epoxy resins, drying oils, and natural rubber, have good wetting and adhesive properties, whereas others, like butyl rubber, polyethylene and polyvinylchloride resins, are inferior in these respects. In practice, experience has shown that some can be used as glues and others cannot, depending on what surfaces are to be joined. If fillers are dispersed in the resin (e.g. pigments, wood dusts, glass or organic fibers), the binding qualities are very important. A strong structural plastic, rubber tire, or paint film can be obtained only if the resinous continuum is a good adhesive between the dispersed filler bodies incorporated in the resin. If the adhesion is good and the filler is properly chosen, the heterogeneous composition can have greater toughness and

strength than is possessed by the unmodified resin itself. When used in binders, a filler is either *inert*, that is, it causes no degradation of plastic properties, or *reinforcing*, when it actually improves the properties of the resinous mass. When the wetting and adhesive properties of the binder are inferior for particular fillers, it may be impossible to compound a homogeneous mixture, or at best the strength of the mixture is inferior to unmodified resin.

Binding agents may be regarded as adhesive liquids of very high viscosity. The chemical and mechanical properties of the adhesive, paint or plastic using such binding agents depends largely on the resistance the resin has to chemical deterioration and upon its viscoelastic properties. Since the binding agent is the continuous medium in any combination with fillers, it largely determines the properties of the mass even though it may be present in minor proportions. For example, a rubber tire may contain less than 50 percent of rubber, and many plastics and paints may contain less than 20 weight percent of natural or synthetic resin.

A great number of commercially available resinous materials have binding properties; for example, casein glues, drying oils, natural and some synthetic rubbers, polyvinylacetate, epoxy resins, and many others. The number of commercial resins lacking notable binding properties is few, for example, some vinyl polymers (particularly the polyfluoroethylene types), polyethylene, polystyrene, and isobutylene polymers. Where binding properties are inferior, the versatility of the resin as a component of commercial plastics or coatings is very limited and its use as an adhesive is virtually nil.

WILLIAM VON FISCHER AND E. G. BOBALEK

Cross-references: *Adhesives; Rubber*

BIOCHEMISTRY

The term "biochemistry," which deals with the chemistry of living things, means now about what "organic chemistry" meant before Wohler, whose synthesis of urea (1828) marked a turning point. Up to that time there was "mineral chemistry" which dealt with minerals, and "organic chemistry" which dealt with the chemistry of organisms. Organic chemistry has now come to have a much more restricted, and in a sense an expanded, meaning the chemistry of carbon compounds—and biochemistry encompasses not only the organic chemistry of living things, but the inorganic chemistry as well—the latter a very important subdivision.

Biochemistry includes in its purview all of the major branches of chemistry as they are related to living things. Thus a biochemist may be interested in any one of a number of broad topics—the physical chemistry of living things, the colloidal chemistry of living things, the electrochemistry of living things, catalysis in living things, photochemistry as it applies to living things, e.g., photosynthesis, etc. He may use all sorts of tools: microanalysis, spectroscopic analy-

sis of various types, electroanalysis of different sorts, colorimetry, turbidimetry, isotopic tracer techniques, in short, almost any technique that is used by chemists in any area. Preparation for biochemistry therefore demands a sound training in all the fundamental branches of chemistry and a good foundation in mathematics and physics. Since the material studied is biological, a grasp of the essentials of biology is also needed.

The immediate forerunner of biochemistry as it is known today is the "physiological chemistry" as it has been taught for several decades in medical schools. This, of course, has its center of interest in mammalian and human biochemistry with more or less emphasis on clinical and pathological findings. Plant Physiology is another field closely related to biochemistry, but its development from the chemical standpoint has been relatively slow, partly because there has been no one kind of plant organism on which everyone in the large field would willingly focus attention.

In the earlier development of biochemistry the emphasis was necessarily upon the topic: the composition of living matter. This, of course, was and is fundamental, and until a substantial storehouse of information and insight accumulated in this area, there was no opportunity to study some of the more absorbing problems related to how organisms live. The development of biochemistry in this area is therefore intimately tied to advances in the fields of protein, carbohydrate and lipid chemistry as well as the chemistry of numerous miscellaneous substances which also enter into the make up of living things.

Earlier books and treatises on biochemistry (whether called by this name or not) were often content to deal with the "straight chemistry" of cellular constituents and excretion products and leave to physiologists or others speculation regarding how these constituents functioned and why they were present. In the course of the development, however, particularly in the past 25 years, there has been an increasing interest in the topics: Nutrition and Metabolism.

Having learned in earlier decades something about the composition of living matter (there is, of course, still much to be learned in this area), biochemists have become engrossed in the question: What do organisms need in their food? For different types of organisms the answer to this question may be very different. Some organisms such as single-celled algae, for example, are able to utilize the energy of sunlight for building up organic matter and do not require in their food any energy-yielding organic material whatever. Others such as molds, as well as certain bacteria, have relatively very simple organic requirements. Sometimes a form of carbohydrate is the only organic substance needed. In all such cases it is a mistake to think of the organisms as simple. Indeed, they must possess a most intricate mass of synthetic machinery because they contain in their make-up a wide assortment of organic materials—carbohydrates, lipides, proteins, including those in cell nuclei, vitamins, etc.—all of which must be built up from relatively simple starting materials.

Such organisms, however, have mineral requirements which are absolute and fairly numerous. Some elements are needed in relatively large amounts, others in minute traces. No organism so far as we know is able to bring about a transformation of one element to another; if molybdenum, for example, is an essential cell constituent for a particular organism, it must be supplied by food. Investigations of trace element requirements can be carried out with greater ease in organisms which have simple organic requirements than with those (e.g. mammals) which require complex organic food. In general, insofar as evidence is available, there is a high degree of unity in the biological kingdom, and a number of the trace elements are known to be needed alike, for a wide spectrum of organisms from single-celled plants to the most complex multicellular animals. At the other end of the biological scale, so far as *organic* food requirements are concerned, are such organisms as mammals which need to be supplied a multiplicity of organic materials of diverse nature without which they cannot live.

It is well to call attention also to the fact that various organisms which have a complex life history may have very different nutritional requirements at different stages in their development. For example, insects may, at the larva stage, have very exacting and complicated requirements for growth and development, but after they become adult flies, for example, they may be able to subsist on a very simple energy-yielding fare. Similar observations apply to typical seed plants. We may think of green plants, since they are capable of carrying on photosynthesis, as having very simple nutritional requirements. In the life history of a seed plant, however, there is a time—before its photosynthetic apparatus is developed—when its requirements may be highly complex. A typical seed, besides carrying a partially developed embryo, carries a store of organic material, carbohydrates, fats, proteins and vitamins, which supply the developing embryo with what it needs for early development. The needs at this stage may be comparable in complexity to those of mammals.

Nutrition has been studied most thoroughly as it applies to young mammals, notably weanling rats. Of the various types of organic compounds found in the tissues, it is notable that certain ones must be supplied in the foods, while others need not be. Thus while carbohydrates are from the quantitative standpoint a most important food for mammals, there appears to be no obligatory requirement for carbohydrates. Fats and phospholipides, particularly the latter, are highly important tissue constituents, yet young mammals can thrive without anything of this nature being supplied in the diet, with the exception of small amounts of certain unsaturated acids: linoleic or linolenic acids. Proteins as such are not required by young mammals, but certain essential building stones are: histidine, lysine, tryptophan, phenyl alanine, leucine, isoleucine, threonine, methionine, valine. Nucleic acids, while playing an extraordinary role in cell reproduction and activity, are quite dispensable nutritionally for young ani-

mals. At this point it may be well to mention that requirements for growth in mammals and fowls are more exacting and deficiencies are easier to demonstrate in the early stages of growth than at or near maturity. It cannot be assumed that in mammals the nutritional needs are the same throughout the life span.

A vast new area in nutrition has developed, mostly in the last half century, in the discovery of vitamins. These nutritionally required substances, which often play catalytic roles, are discussed more fully in a section devoted to that subject.

A major part of the subject of biochemistry is that devoted to *metabolism*. This has to do with all the chemical events which transpire from the time food material is taken in by the organism until it is made use of and the waste products are eliminated. In mammals, for example, digestion and absorption are preliminary steps, followed in the body proper by an intricate series of degradations, syntheses, transformations, and oxidations, all of which may involve cyclical processes. These events are distinctive for each substance metabolized and are often localized with respect to organs, tissues and types of cells involved. Since there are numerous substances entering into metabolism, the subject as a whole is vast.

Chemical reactions taking place within organisms are most often mediated by specific catalysts built up by the organism for the purpose. Even such a commonplace reaction as the decomposition of carbonic acid into carbon dioxide and water is mediated by a specific enzyme catalyst, carbonic anhydrase. Into the make up of these enzymes go the essential protein building stones, and often vitamins and trace elements. Carbonic anhydrase, for example, contains zinc, and one basis for the need of this element is its presence in this indispensable enzyme. The number of enzymes produced by mammalian organisms is large. For example, instead of two or three enzymes being required for protein digestion, there are perhaps dozens. While we often think of enzymes as being present in minute amounts, this is not always the case, and it is probable that a substantial part of the total protein in a mammalian body has enzymatic functions. Many enzymes and apoenzymes (discussed elsewhere) have been isolated in the form of purified proteins.

One of the large areas of metabolism which is as yet relatively obscure has to do with the interrelations between *hormones* and enzymatic processes. Hormones (which are discussed more fully elsewhere) are produced in various localities and are transported by the blood to their site or sites of action. Though some starts have been made toward elucidating how they perform their functions, this section of biochemical history is largely yet to be written. It may be presumed in many cases that they play a catalytic role, but this is difficult to demonstrate. Enzymes can be shown to be catalysts by the most rigorous type of chemical experiment. Hormones, however, usually exhibit their effects within living organisms and

when they are studied for direct chemical effects *in vitro* the results are generally negative.

A relatively new area of investigation which impinges directly upon problems of nutrition and metabolism is that of biochemical genetics. It is now apparent, on the basis of numerous studies, that the ability to produce the multiplicity of specific enzymes contained in an organism is transmitted through the genes, just as are the capabilities for producing specific morphological structures. Different species of animals, for example, are different with respect to their metabolisms, because of differences in their inherited genes. These in turn also make them different in their nutritional needs. Guinea pigs, monkeys and humans require ascorbic acid in their food because the guinea pig, monkey and human genes do not transmit the capability of producing the enzymatic machinery necessary for its synthesis. Rats and dogs, for example, have transmitted through their genes the ability to produce ascorbic acid as needed. In view of the complete dependence of enzyme production on genic transmission, it becomes increasingly certain that substantial differences in metabolism and in nutritional needs exist not only between different species of animals, but between different strains and individuals within the same species. This finding has far-reaching potentialities in relation to both the susceptibility to and the treatment of disease.

Biochemistry is rich in intriguing problems. How is stored chemical energy transformed into mechanical energy when muscles work? Just what are nerve impulses and what chemical reactions underlie their variable speed of propagation? What chemical mechanisms are involved in the process of photosynthesis and can these be duplicated artificially? What chemistry is involved in the process of vision? What are the details of the enzymatic process whereby bioluminescence (cold light) is produced? What chemically is back of the process of differentiation, whereby parent cells produce progeny which are entirely different from the parents? How and why do cancer cells arise, and what keeps them from arising much more often than they do? When specific drugs act upon the body, what phases of metabolism and what enzyme systems do they influence?

Answers to these questions and many others are being continually sought, and the successes and partial successes which have resulted make the field of biochemistry attractive to larger and larger numbers of scientifically inclined men and women.

ROGER J. WILLIAMS

Cross-references: *Nutrition, Vitamins, Hormones, Enzymes*

BISMUTH AND COMPOUNDS

In the middle ages Europeans had recognized bismuth as a specific element and referred to it as *wismut* which was later Latinized to *bismutum*. Bismuth occurs in the earth's crust in about the

same abundance as silver. Although it is found as native bismuth, the major portion is combined in ores. The minerals are widely distributed in the world but in small quantities. An estimated 2,000,000 to 4,000,000 pounds of bismuth were produced annually in the world over the last decade. 40-50% of this is refined in this country.

The primary source of bismuth in the western hemisphere is as a by-product of copper and lead smelting and refining. The bismuth occurs in ores with these metals and remains with the metals after smelting. Bismuth is recovered from copper in the anode slimes during the electrolytical refining and the procedure for handling the slimes is such that the bismuth is collected in lead. Bismuth is removed from lead during the refining by the Betterton-Kroll process, which depends upon the formation of calcium-bismuth and magnesium-bismuth compounds whose high melting points and lower density permit them to be liquated from the lead bath. The enriched bismuth dross is freed of calcium, magnesium and lead by chlorination.

Bismuth will fracture as a brittle, crystalline metal having a high metallic luster with a pinkish tinge. As a member of Group VB of the Periodic Table, it is in the same subgroup as arsenic and antimony.

Atomic No.	83
Atomic Weight	209
Density—20°C g/cm ³	9.80
Density -271.3°C g/cm ³	10.067
Density 20°C lb/in ³	0.354
Atomic Volume $\frac{\text{cu-cm}}{\text{g-atom}}$	21.3
Melting point—°C	271.3
Boiling point—°C	1420
Specific heat—20°C cal/g/°C	0.0294
Heat of fusion - cal/g	12.5
Vapor pressure—540°C	10 ⁻⁴ mm
840°C	1 mm
1200°C	100 mm
Crystal form - Rhombohedral	
$\Lambda = 4.7361 \text{ \AA}^\circ$	
Axis angle - 57° 14.2'	

Bismuth is one of the few metals (antimony and gallium the others) which increases in volume on solidification, this expansion being 3.32%. The thermal conductivity of bismuth is lower than any metal with the exception of mercury. The most diamagnetic of all metals, bismuth has a mass susceptibility of -1.35×10^4 .

The low absorption cross section of bismuth for thermal neutrons has focused attention upon it as a possible coolant for nuclear reactors.

Bismuth alloys with a number of other low-melting elements to form a group of alloys commonly referred to as "fusible alloys". The following table gives a number of the common eutectic compositions and melting temperatures:

System	Composition	Eutectic Temperature
Cd-Bi	60 Bi	144°C
In-Bi	33.7 Bi	72°C
	67.0 Bi	109°C
Pb-Bi	56.5 Bi	125°C
Sn-Bi	58 Bi	139°C
Pb-Sn-Bi	52 Bi 16 Sn 32 Pb	96°C
Pb-Cd-Bi	52 Bi 4 Cd 40 Pb	92°C
Sn-Cd-Bi	54 Bi 20 Cd 26 Sn	102°C
In-Sn-Bi	58 Bi 17 Sn 25 In	79°C
Pb-Sn-Cd-Bi	50 Bi-10 Cd-13.3 Sn-26.7 Pb	70°C
In-Pb-Sn-Bi	49.4 Bi 11.6 Sn-18 Pb-21 In	57°C
In-Cd-Pb-Sn-Bi	14.7 Bi-5.3 Cd-8.3 Sn 22.6 Pb-19.1 In	47°C

Fusible alloys e.g. Wood's metal, are used in a number of ways for such safety devices as safety plugs, compressed gas cylinders, automatic fire sprinkler systems and fire door releases. Some of the bismuth alloys have other unusual properties such as low liquid to solid shrinkage and expansion in the solid state. These properties have led to their use for gripping tools, punches and parts to be machined. Bismuth may be melted and cast in the same manner as lead, but its low ductility does not permit working at ordinary temperatures. At higher temperatures (above 225°C) it becomes more plastic, permitting a limited amount of shaping.

Two sets of compounds will form in which bismuth is trivalent and quinquivalent. The trivalent compounds are the more common. Bismuth does not readily form oxides at ordinary temperatures. The metallic luster is retained for a long period of time. Bi_2O_3 is the best defined of the oxides, the existence of others being questioned. The compounds of bismuth with the halogens are of the form BiX_3 . They may be readily formed by dissolving the bismuth in nitric acid and adding a soluble halogen salt. The salts of trivalent bismuth hydrolyzed in water to insoluble basic salts precipitating the oxysalt. The best solvent for bismuth is nitric acid. From the concentrated solution the bismuth nitrate pentahydrate is formed. Concentration of this solution by evaporation will form the nitrate. The subnitrate is prepared by the hydrolysis of bismuth nitrate between temperatures of 30° to 70°C. Bismuth subcarbonate is prepared from the bismuth subnitrate by adding sodium carbonate. Both bismuth subcarbonate and bismuth subnitrate are used for medicinal purposes.

HERBERT E. HOWE

BITUMENS, see ASPHALT

BLEACHING

A method of whitening fabric by treatment with selective chemicals such as hydrogen peroxide, chlorine, or oxygen. Raw cotton as it comes from the cotton gin consists mainly of cellulose. In addition to the cellulose are hygroscopic moisture and natural impurities. Experimental work regarding the natural impurities show the presence

of at least five different compounds which may be classified as follows.

(1) *Cotton wax*: a wax-like substance, insoluble in water and quite inactive chemically. A thin coating of the substance probably produces the well known water-repellent effect characteristic of raw cotton. (2) *Fatty matter*: a fatty substance that appears to be margaric acid or a mixture of palmitic and stearic acids. This portion is readily removed by the action of alkalis. (3) *Coloring matter*: nitrogenous matter possessing a brown color which is present in small quantities, giving raw cotton a light brown or creamy color. This coloring matter is removed by oxidation. (4) *Pectic acid and its derivatives*: Pectic acid is usually present as calcium or magnesium pectates. (5) *Albuminous matter*: The pectic acid compounds and the albuminous matter are removed by alkalis.

The presence of these impurities does not interfere with the manufacturing processes, and since it is general practice to manufacture cloth or knit goods from raw cotton, these compounds appear in the woven or knit fabric. In the manufacturing process various compounds (size, oil and dirt, etc.) are added to the cotton either by accident or design. Size consists of starch or gum plus fatty matter or hydroscopic agents. In bleaching cotton piece goods these impurities, both natural and added, must be removed so that the goods may be sold white; thus they may be dyed light, bright colors or may be printed.

There are two common methods in use for bleaching cotton piece goods: (1) the hypochlorite or chlorine bleach and (2) the peroxide bleach. For many years the hypochlorite bleach was used almost exclusively, but during the past thirty years it has been replaced by the peroxide bleach. Today it is estimated that this is used on over 85% of the cotton cloth that is bleached. The hypochlorite bleach is a long process consisting of alkaline boils, acid treatments and treatment with sodium hypochlorite to remove the impurities in the cotton.

If a clear thread finish is desired the goods are then singed. Singeing consists in passing the goods over red hot metal plates or rolls or passing the goods through a gas flame. The object of this step is to remove the fuzz from the surface of the fabric.

After the singeing operation the goods are desized. The object of this process is to remove the starch used in the warp size from the cloth. Desizing is carried out by the use of enzymes that will solubilize starch.

The desized material is then packed evenly into a kier. A kier is a wrought iron cylinder closed at the top and bottom and provided with a pump or other device for circulating the solution through the cloth. The kier operates at 12-15 psi. In this step the cloth is boiled in a solution of 2½ to 3% sodium hydroxide (on weight of material) plus a small quantity of a sequestering agent and a wetting agent. This boil lasts eight to twelve hours and in some cases it may be repeated using a fresh solution. The cotton wax, fatty matter, albuminous matter and pectic acid derivatives are removed in this step. This is an important step

in the bleaching process, since complete removal of these impurities is necessary to obtain a good bleach.

The cloth next passes through a 1½°-2° Twichell solution of sodium hypochlorite then through squeeze rolls and into a J-box where it is stored for 1 to 1½ hours. A J box is a chute made in the form of a letter J. In this bleach it is made of wood and is of open slat construction so that the air can come into contact with the cloth saturated with sodium hypochlorite. In this step the sodium hypochlorite breaks down, giving chlorine and oxygen. The chlorine reacts with water, giving oxygen. The oxygen given off acts as a bleaching agent. This breaks down if the sodium hypochlorite in this step is very slow. The cloth leaving the J box after storage is run through a washer. The object of this wash is to remove the excess sodium hypochlorite.

The acid treatment that follows consists of passing the material through a ½% sulfuric acid solution, through squeeze rolls and into a J-box similar to the one used in the sodium hypochlorite treatment. In this step we get the greatest bleaching action. The sodium hypochlorite remaining in the cloth is broken down by the sulfuric acid, giving chlorine and oxygen. The chlorine reacts with water to give oxygen and the oxygen bleaches the cloth.

The wash after this step is to remove the chemicals left in the cloth. It is difficult to remove the last traces of chlorine by washing, so the chlorine is neutralized by passing through a solution of sulfurous acid. The chlorine reacts with the sulfurous acid to form sulfuric and hydrochloric acids, which are readily removed by washing in water.

Wool is seldom bleached since it is not possible to obtain a pure white as in the case of cotton. If necessary it may be bleached by (1) the reduction bleach or (2) the oxidation bleach. The oxidation bleach is permanent, but wool bleach by the reduction bleach returns to its original color upon exposure to the air. The reduction bleach is carried out by treating the wool in a solution of sulfurous acid (obtained from sulfuric acid and sodium bisulfite) or by exposing wet wool to the action of sulfur dioxide.

The peroxide bleach consists of treating the wool 12-15 hours in a one to two volume hydrogen peroxide solution that has been brought to pH 7.2-1 with sodium silicate at a temperature of 120°F. This treatment is followed by a wash and a bath of dilute acetic acid to neutralize any alkali.

Other cellulose fibers, both natural and manufactured, are bleached by methods similar to cotton, while the protein fibers are bleached like wool. Of course the process used must be modified to suit the fiber being processed and the impurities present in it. That is, natural impurities are not present in manufactured fibers. Synthetic fibers are bleached with hydrogen peroxide similar to wool or with sodium chlorite.

CHARLES L. HOWARTH

Cross-references: *Textile Chemistry, Chlorine, Peroxides*

BLOOD

Chemical Composition. Blood is a circulating fluid tissue of solid particles dispersed in colloidal plasma. It is opaque from the enormous number of cells in suspension, red from the erythrocytes which carry the hemoglobin, viscid from the high protein content. When blood is centrifuged or clotting prevented, the solid particles separate from the lighter fluid plasma. Its yellowish coloration is due to traces of carotene and xanthophyll derived from the diet, and to bilirubin from degraded hemoglobin. Blood plasma serves as the main transport medium of nutrients from the alimentary tract to the tissues, of metabolites from one tissue to another, of hormones from their organs of origin to target tissues, and of end products from the sites of their production to excretory organs.

Most molecules carried from one part of the body to another travel on a protein. Lipides are bound as α - and β -lipoproteins. Polysaccharides, hormones, metals, drugs, dyes are all protein-bound. The chemical composition of blood plasma in equilibrium with interstitial fluid as representative of extracellular fluids. The concentration of a given component reflects the state of metabolism, i.e., normal or abnormal formation, utilization or excretion of that substance. Deviations from normal levels are due to some imbalance between the rate of entrance into or removal from the blood stream. These variations in plasma compounds are determined by micromethods to elucidate the diagnosis, prognosis and treatment in every branch of medicine.

TABLE 1. PHYSICAL PROPERTIES OF HUMAN BLOOD

Blood volume = 7-8% of the entire body weight
70-80 ml per kgm \approx 5 liters of blood in 70-kg adult (calculated from the total volume of plasma or cells and the plasma/cell ratio determined by the hematocrit).

Blood volume = 72 ml/kg \approx 2.9 liters/sq. meter

Plasma volume = 40 ml/kgm \approx 1.5 liters/sq. meter

Reaction of blood and plasma = pH 7.35-7.45; cell contents pH 7.1

Specific gravity of blood = 1.056 and of plasma 1.026

Water content of blood = 83%, of plasma 94% of corpuscles 65%

Plasma osmolar concentration = 320 M Osm/liter

Osmotic pressure of blood = 7.0 atmospheres

Plasma colloid osmotic pressure = 24 mgm Hg \approx 0.03 atm.

Hematocrit = 45% cells

Specific gravity of

plasma = 1.0253-1.0287

serum = 1.0245-1.0275

corpuscles = 1.0880-1.0889

Refractive index of serum 17.5°C = 1.3490-1.3507

Viscosity of plasma = 0.5-0.6

(Water serum = 1.7-2.0

= 1) blood = 3.6-5.4

Freezing point depression of serum = 0.550

Sedimentation rate

of red cells = 0.5 mm/hr. newborn

3.3 mm/hr. male

7.4 mm/hr. female

44.9 mm/hr. pregnant female

Regulatory Mechanisms. The external environment is heterogeneous but the internal environment homogenous and remarkably constant by the intervention of many regulatory and compensatory mechanisms, especially acid-base balance, osmotic pressure, concentration of solutes and ions, nitrogen equilibrium, body temperature, metabolism, etc. The maintenance of life depends upon these physicochemical processes, controlled by balanced equilibria of the many homeostatic mechanisms. But the constancy of the internal environment is not absolute if stresses imposed upon the system become too great. Homeostasis fails, with disastrous results to the organism; thus a deviation of H^+ ion concentration from the normal pH 7.4 to 7.0 or 7.8, a change of calcium from 10 mgm to 5 or 15 mgm/100 ml, an alteration of blood sugar from 100 to 30 or 1,000 mgm/100 ml may cause loss of consciousness or even death.

Plasma proteins regulate the distribution of water between the two compartments of the extracellular fluid, aqueous exchanges across capillary walls and filtration processes through renal glomeruli. The fluid compartments of the body comprise 75% of the body weight of infants and 60% in adults. In the former, this is divided between 5% blood plasma, 25% interstitial fluid and 45% intracellular fluid in terms of total weight, while in the adult the proportions are 5, 15 and 45% respectively. The body's ability to maintain constant temperature is largely due to the high specific heat of water. Heat produced in the course of metabolic reactions in the cells is distributed throughout the body fluids by the blood stream to equalize the temperature in various tissues. Blood circulation at the body surface in the skin and lung alveoli permits loss of excessive heat by radiation and evaporation. Formed elements in the blood bear the body's defenses against invading injurious agents. Even blood coagulation is a protective mechanism against undue loss of blood following trauma.

Buffer Systems. The pH of body is kept within proper limits by the buffer action of the blood, maintained by the lungs, which remove CO_2 , and the kidneys which excrete the cations H^+ and NH_4^+ and the anions OH^- and HPO_4^{2-} . The chief blood buffers are the proteins of the erythrocytes and plasma, whose isoelectric points are all acid, i.e., hemoglobin pH 6.8, albumin 5.5, globulin 4.4. At the pH of blood these proteins have their terminal amino acid groups free, capable of accepting H^+ as anions. The emergency carbonate buffersystem $HC(O_3)^- + H^+ \rightleftharpoons H_2CO_3$ and the phosphate buffer system $HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$ protect against marked or prolonged acid-base disorders. The plasma alkaline reserve 55-75 ml CO_2 per 100 ml represents the available buffer capacity to protect the body against acidosis, i.e., fall in pH below 7.3. Circulating blood pro-

fects tissues from disadvantageous changes in the pH on the alkaline side by the protein buffers and on the acid side by the bicarbonate and phosphate buffers.

Hemoglobin buffers produce their maximum effect at pH 7.7, close to the normal pH of blood. But plasma proteins bind base so firmly as to contribute less than one-tenth of the total buffer action of blood. Bicarbonate buffers at pH 7.4 show a ratio $\text{BHC}(\text{O}_3):\text{H}_2\text{C}(\text{O}_3)$ of 20:1, at its minimum efficiency; and a ratio of $\text{BHC}(\text{O}_3):\text{H}_2\text{C}(\text{O}_3)$ equals one at pH 6.1 at its maximum efficiency. Consequently, any shift of the blood in the acid direction progressively increases the bicarbonate buffer efficiency a fortunate circumstance for the human body. With the phosphate buffers the same improvement maintains, since the ratio $\text{B}_2\text{H}_2\text{P}(\text{O}_4):\text{BH}_2\text{P}(\text{O}_4)$ equals 1 at pH 6.8.

The acid-base mechanism has been further clarified by the Brønsted-Lowry concept. The ions Na^+ or K^+ are viewed by the clinician as "basic" and Cl^- or PO_4^{3-} as "acidic". Actually Na and K ions are not bases and chloride and phosphate ions not acids. The only components involved in acid-base balance at physiological pH are the proteins, i.e., hemoglobin, oxyhemoglobin and plasma protein, bicarbonate ion, carbonic acid, primary and secondary phosphate ions. The role played by Na, K and Cl ions in the buffer capacity of blood is that of electrical make weights to keep the blood at electroneutrality.

Formed elements. Erythrocytes or red cells dispersed in plasma are not truly living cells, but are composed of 65% water, 32% hemoglobin and 3% protein and lipid stroma. They are circular, nonnucleated biconcave discs, markedly elastic, properties ideal for their functions to absorb oxygen rapidly in the lungs, to pass through the smallest capillaries without damage and to give up O_2 rapidly to the tissues. Normally, the average red cell count is about 5 million per c.mm. The surface area of the red cells is about 3000 sq. m. or 1500 times the surface area of the body. The life span of a normal red cell is about 120 days while the usual rate of replacement is about 0.8% per day.

The leucocytes or white cells are living cells with nuclei formed for protection of the body from disease. They are rich in nucleoproteins and lipides. Lymphocytes contain relatively large amounts of γ -globulin, the antibody being liberated upon lysis. Granular cells contain glycogen and show active glycolytic metabolism. Basophilic granules contain alkaline phosphatase, cytochrome-C and cytochrome oxidase. The 11-oxygenated adrenocortical hormones accelerate lymphocyte and depress eosinophile production.

The platelets are oval bodies extruded from giant megakaryocytes in red bone marrow. They contain proteins and phospholipides, especially cephalin. Upon lysis they liberate several substances essential for blood clotting—thromboplastin; serotonin, a vasoconstrictor; factor I an accelerator for the transformation of prothrombin to thrombin; and factor II an accelerator for the conversion of fibrinogen to fibrin by thrombin. Platelets not only coagulate but re-

tract shed blood and repair damaged blood vessels. Normally, the platelet count is 250,000–500,000 per c. mm., with a survival time of about 3 to 5 days, a volume of 5 c. microns, diameter 2 microns and 0.5 volume per cent in the blood.

Erythrocyte Hemoglobin. The red cell's most important component, hemoglobin, remains stable without undergoing degradation or resynthesis during the life of the cell. Hemoglobin is composed of a pigment heme bound to precursor substances. The synthesis of heme in the body requires adequate supplies of porphyrin and of iron. Studies with radioactive carbon show that glycine and acetic acid are necessary to make up the porphyrin nucleus, while acetoacetic acid, proline, hydroxyproline and tryptophan are additional building units required. Iron is absorbed in the body in ferrous form from available iron-containing foods or derived from the breakdown of effete red cells in the spleen. The synthesis of globin in the body requires ten essential amino acids obtained from adequate dietary protein, although amino acids are always available from the breakdown of autogenous protein at the body's expense. As the result of the union of the porphyrin derivative and the protein, the heme is activated and thereby enabled to combine reversibly with molecular oxygen to form oxyhemoglobin, without change in iron valence. The hemoglobin molecule, contains four heme molecules bound to one globin molecule, revealing a molecular weight of 68,000. The porphyrin is bound to the protein via the carboxyl group of the propionic acid substituents. The ferrous iron is bound in coordinate linkage to the four nitrogen atoms of the porphyrin. The fifth link is bound to the imidazole nitrogen of the histidine of globin. The sixth link binds oxygen reversibly.

Oxygen carried from the lungs by hemoglobin is passed on in tissue cells to cytochrome oxidase, a heme enzyme which activates oxygen to accept electrons from the cytochromes which are in the final position of the oxidative chain. Their iron atoms are reduced from the ferric to the ferrous state by accepting electrons from the substrates of the dehydrogenating systems. They are then oxidized by molecular oxygen to which they in turn transfer electrons. By repeated alternate oxidation and reduction, small amounts of these cytochromes participate in the oxidation of enormous quantities of material in the cell. Heme compounds are thus concerned with transport and storage of oxygen, with making oxygen available to the cell, and with the oxidation of cellular constituents, all basic energy-yielding reactions of living matter.

Several types of hemoglobin A, C, D, F, S and others are recognized by electrophoresis and chemical behavior. Fetal (F) hemoglobin is a biologic provision for survival under the low oxygen tension of fetal life. It absorbs O_2 at low concentrations more effectively and releases CO_2 more readily than adult (A) hemoglobin. At birth, when pulmonary respiration replaces the placenta, A displaces F hemoglobin completely by the sixth month of life. Hemoglobin S is inherited by 8% of negroes as sickle cell anemia developed after the

sixth month when S supplants F. Hemoglobin C is also inherited, producing sickling target cells, hemolytic anemia, arthralgia and splenomegaly. Hemoglobin D is a third variety of hereditary sickle cell anemia.

Plasma Proteins. The total plasma protein concentration ranges from 6.0 to 8.0 gms.%, predominating in two principal groups—serum albumins and serum globulins. Of the albumins, representing about $\frac{2}{3}$ of the total protein, only mercaptalbumin has been isolated. Of the globulins, formerly divided into alpha, beta and gamma fractions, each of these fractions have fractions of their own. Fibrinogen remains a single component. Thus far, electrophoretic determinations have isolated 40 proteins representing about 90% of the total plasma protein. The last elusive 10% represents twice that number present in such small quantities as to make separation difficult.

The liver normally produces albumins, fibrinogen, prothrombin and about 80% of the globulins. The spleen, lymphoid elements and other sites of the reticuloendothelial system produce beta and gamma globulins. Isotopic techniques with tagged amino acids reveal that an individual normally synthesizes and degrades 15-20 gms. plasma protein daily. The life span varies with the protein, from 12 to 30 days, although the computation is complicated by the interchangeability of proteins from plasma, lymph and tissues. The source of all body protein is the adequacy of the daily diet. When inadequate, the individual goes into negative nitrogen balance. Tissues and organs are first to suffer and plasma protein the last. When plasma proteins are depleted by starvation, hemorrhage or renal disease, the chief ions Na^+ and Cl^- permeate the capillary walls, accumulate in the tissues and produce local edema. The fall in blood volume cannot be replaced by isotonic saline but by a suitable colloid, particularly plasma, to increase the effective colloid osmotic pressure.

Plasma Nonprotein, Nitrogenous Compounds. Most of the heterogenous nitrogenous compounds are either metabolic intermediates transported to tissues from the site of absorption or proceeding from the tissues as end-products for excretion. None are precipitated by protein-precipitating agents. Of the total nonprotein nitrogen 50% is represented by urea, 25% by free amino acids and the remaining 25% by a large number of metabolic compounds of varied origin. Urea is the chief nitrogenous end product of protein metabolism, representing the amino groups in excess of the requirements for synthesis of nitrogenous compounds. Urea is formed in the liver from amino acids, released into the blood stream and excreted in the urine. It diffuses readily through all cell membranes and capillary walls, and therefore occurs in all fluid compartments, cerebrospinal fluid, gastrointestinal secretions and perspiration. Free amino acids comprise a metabolic pool for the dynamic equilibria between plasma, tissues and hemoglobin embodying amino acids from ceaseless deamination and reamination. The plasma concentration of free amino acids is thus the resultant of these catabolic and anabolic processes.

Uric acid is the primary end-product of purine metabolism, but the plasma level is only slightly affected by purine-rich foods. It is formed in the liver, released in the blood stream, and excreted in the urine, but is the first nitrogenous constituent to be retained in nephritis. Creatin is the anhydride of creatinine, the metabolic end-product formed in muscle, transmitted into the circulation and excreted in the urine. Ammonia nitrogen is maintained in insignificant amounts for the toxic NH_4^+ is rapidly converted into urea in the liver.

Plasma Carbohydrate. Dextrose is the circulating unit of energy currency in blood. It is the chief reducing substance although the material determined by the usual reduction methods includes other circulating reducing substances 15-30 mgm.%. The nondextrose reducing substances in blood are glutathione and ergothioneine, more abundant in cells than in serum. The range of normal blood sugar values in infants is from 60 to 100 mgm.%, while in adults it is 70 to 120 mgm.%.

Pentose occurs as nucleosides and nucleotides. Polysaccharides and glucosamines include a variety of substances composed of galactose, mannose, glucosamine and mucoprotein. Pyruvic and lactic acids increase during strenuous exercise, thiamine deficiency and congestive heart failure. Lactic acid originating from muscle glycogen during the contraction process is transported to the liver for reversion into glycogen or dextrose.

TABLE 2. CARBOHYDRATE COMPONENTS OF BLOOD PLASMA

Carbohydrate	mg. 100 ml
Dextrose	70-110
Fructose	5-9
Lactose	0-2
Polysaccharides	90-140
Glucosamine	50-90
Lactic acid	5-20
Pyruvic acid	0.4-2
Citric acid	1.5-3

Plasma Lipides and Related Compounds. The lipid content of plasma varies widely in health, even in the post-absorptive state. It includes neutral fats and fatty acids, phospholipides, cholesterol and its esters, cerebroside and sterols. Some lipides are structural, forming an integral part of the cell's architecture, while others are functional, undergoing complete oxidation reactions in metabolic processes or stored as neutral fat. An increase in blood fat due to chylomicrons occurs shortly after a high fat meal, returning to the fasting level in 3 to 6 hours. If the lipid concentration is high, plasma becomes opalescent. Blood lipides rise during normal pregnancy after the third month, during starvation owing to the mobilization of stored fat and fall subsequently in severe malnutrition. The level of cholesterol tends to rise, advancing age accompanying the development of atherosclerosis.

Ketone bodies, especially acetoacetic acid, beta-hydroxybutyric and acetone occur normally at very

low levels, but increase rapidly during dietary restriction or inadequate utilization of carbohydrate.

TABLE 3. LIPIDES, KETONES AND BILE IN PLASMA

Components	mg./100 ml
Total lipide	385 675
Neutral fat	0 260
Phospholipids	110 250
Lecithin	80 200
Cephalin	0 30
Sphingomyelin	10 50
Cholesterol	140 260
Ester	90 200
Free	40 70
Fatty acids	110 485
Ketone bodies	0.2 0.9
Bile acids	0.2 3.0

Plasma Anion-Cation Balance. Blood contains a variety of anions and cations of different concentrations, but the total number of ionic positive charges is balanced by an equivalent number of negative charges. Total base embodies the inorganic cations of serum, excepting NH_4^+ , i.e., sodium, potassium, calcium and magnesium. Potassium ions predominate in the cells and sodium in the plasma and extracellular fluid. Calcium is present in serum as calcium ions and calcium proteinate and completely absent in the cells. The calcium ion concentration of serum is about 5 mgm.% and the rest is bound to albumin and globulin. Magnesium is distributed between serum and cells.

The total anion content of plasma includes bicarbonate, chloride, phosphate and sulfate. The total CO_2 in blood represents that present in bicarbonate and that contained in carbonic acid. Chlorides in whole blood are more variable than those of serum and corpuscles due to the ever changing proportion of cells to plasma. Normally, the ratio of Cl in cells to Cl in serum is about 0.55. Total phosphate consists of phospholipides, inorganic phosphate and organic phosphate esters, the latter found chiefly in the red cells. Inorganic sulfates are evenly distributed between cells and serum.

Trace elements include iron, iodine, copper, lead and a variety of metallic compounds. Iron is contained completely in the erythrocytes. Small amounts of iron in plasma depend on the amount absorbed from the intestinal tract, from hemoglobin destruction and from transport iron en route to and from tissues. β -globulin binds iron in the plasma. Copper is equally distributed between cells and plasma. Iodine is present as hormone iodine, i.e., thyroxine and diiodotyrosine and as inorganic iodide. Blood iodine is an index of thyroid function and of iodine metabolism, yet maintains a more constant level than thyroid iodine. Lead is normally present in very small amounts but values above 0.008 mgm.% must be considered abnormal. Metallic plasma components such as manganese, copper, tin and silver probably serve as coenzymes in metabolism.

TABLE 4. INORGANIC COMPONENTS IN BLOOD PLASMA

Component	mg./100 ml.	m. Eq./liter
Sodium	300-350	132 152
Potassium	14-21	3.6 5.3
Calcium	8.5-11	4.2-5.7
Magnesium	1.7 2	1.4 2.4
Bicarbonate	55-72	24-31
Chloride	340 380	97-108
Phosphate	3 4	2.2 4.2
Sulfate	1 2	0.7-1.5
Iron	0.03 0.18	
Iodine	0.004 0.008	
Copper	0.08 0.16	
Lead	0.008 0.06	

Plasma Enzyme Systems. Blood contains a variety of enzymes which function cyclically in specific metabolic processes. The trace proteins act in conjunction with accessory substances such as coenzyme S, minerals and hormones. The catalytic nature of their action is identical with an elementary life. Oxidation of stable enzymes in plasma protein fractionation is simple, but of unstable enzyme proteins most difficult. Genes determine the presence of enzymes and hormones regulate their reactions.

TABLE 5. STABLE ENZYMES IN BLOOD PLASMA

Enzyme	Activity per 100 ml. Plasma
Amylase	80 180 units
Cholinesterase	130-365 μ l CO_2 /hr
Lipase	0 2 ml. 0.1 N NaOH
Phosphatase, acid	14.0 units in infants
Phosphatase, alkaline	0.5 1.5 units
	2.0 4.5 units in adults

Plasma Vitamins. Experimental studies reveal the role of blood in the transport of vitamins to and from the tissues. Normal concentrations have thus been established for blood plasma preprandially on adequate dietaries.

TABLE 6. VITAMIN CONTENT OF BLOOD PLASMA

Vitamins	μ g./100 ml
Vitamin A	40 400
Vitamin D	1.5-4.5
Vitamin E	900 1900
Ascorbic acid	400-1700
Thiamine	5-10
Niacin	20 150
Riboflavin	2-4
Pantothenic acid	10 35
Pyridoxine	1-18
Biotin	1-2
Folic acid	1.5 5
Vitamin B ₁₂	0.01-0.1

Blood Clotting. The coagulation of blood is the end result of a chain of chemical reactions in plasma involving the conversion of soluble fibrinogen into insoluble fibrin by means of an enzyme thrombin. Fibrinogen is a soluble fibrous globulin synthesized in the liver as long thread-like molecules $900 \times 33 \text{ \AA}$, molecular weight 450,000, vis-

cosity high, and isoelectric point pH 5.5. Fibrin is an insoluble tough plastic protein of molecular weight 50,000 formed as a network of fine threads from the soft hydrogel by syneresis to 10% of the original volume of blood. Thrombin is a soluble albumin enzyme with molecular weight 75,000 which coagulates over 600 times its weight of fibrinogen. Within shed blood chemical reactions of ant clotting compounds occur in the opposing direction, inhibiting the formation of fibrin. The end result of these interactions depends on the concentration of the components and the conditions of the reactions. Clotting will take place only when the rate of production of clotting compounds exceeds the rate of their neutralization by opposing inhibitors.

The first step in the clotting mechanism is the activation of thromboplastin, a protein present in the blood as the inactive thromboplastinogen. When a wound occurs, large amounts of active tissue thromboplastin are liberated into shed blood. The blood platelets in contact with the wound disintegrate and liberate the lipide, which transforms inactive plasma thromboplastinogen into active thromboplastin. The second step in clotting involves the formation of thrombin,—a protein that acts as a powerful enzyme. Normally, intravascular clotting does not occur because in the circulating blood only the inactive precursors of thrombin are present i.e., prothrombinogen and prothrombin. They are formed in the liver from vitamin K as glycoproteins with plasma concentrations at about 20 mg. per 100 ml. However, when blood is shed, the prothrombin complex combines with thromboplastin to form thrombin in the presence of calcium ions as an autocatalytic reaction in which the substance formed accelerates the process. Side reactions include a trace of thrombin formed that disintegrates platelets and thus liberates the lipide further to increase thromboplastin; and that thrombin also converts plasma globulin into serum-globulin accelerators which increase the formation of thrombin.

In the third stage of clotting, fibrin coagulates as an insoluble protein formed from soluble plasma fibrinogen by the action of the thrombin. Fibrinogen is precipitated into profibrin and finally into fibrin. It first appears as needles and then as threads. These entangle the red blood cells, and contract to form a clot, which is at first soft and friable and then becomes tough. Clear yellow serum, rich in thrombin, is then squeezed out. The fibrin serves the clotting mechanism by enmeshing the platelets, which liberate a vasoconstricting principle, by absorbing thrombin to halt the chain reaction and by plugging the wound within and without the vessel wall.

The clotting compounds may be neutralized by inhibiting agents that are normally present in blood. Anticephalin may neutralize some of the thromboplastin liberated when trauma or platelet destruction occurs. Heparin is a polysaccharide of molecular weight 17,000 present in traces in normal blood. It is not a physiologic anticoagulant. But in anaphylactic shock, heparin with an albumin cofactor combines with prothrombin to halt

the latter's transformation into thrombin. This action prevents platelet agglutination and disintegration. The body does not release heparin into the blood to halt thrombosis. But plasma does contain a natural antithrombin albumin X, which converts thrombin into inactive methathrombin. Finally, the plasma in certain types of bleeding develops anticoagulants of unknown nature. Circulating anticoagulants may thus cause rare but specific hemorrhagic diseases.

I. NEWTON KUGELMANN

Cross-references: *Colloid Chemistry, Acids, Bases, pH, Buffers, Proteins, Lipides, Rh Factor, Plasma Volume Expanders*

BOLTZMANN, LUDWIG (1844–1906)

Ludwig Boltzman was born in Vienna in 1844. He studied in Vienna, Heidelberg and Berlin. In 1866 he presented before the Austrian Academy of Sciences a paper on the second law of thermodynamics, and this subject occupied much of his life. He was appointed in 1869 professor of theoretical physics at Graz, but during the next decades he held positions at many universities including Munich, Leipzig and Vienna. Boltzmann's contributions were mainly concerned with the development of the Kinetic Theory of Gases and electromagnetic phenomena (Boltzmann's Law). Between 1891–1893 he published, "Vorlesungen über Maxwell's Theorie der Elektrizität und des Lichtes, 2 vols.". The "Vorlesungen über kinetische Gastheorie, 2 vols., 1896–1898" remains a classic, and stimulated much further research. Between 1880 and 1882 he published a series of papers on the viscosity and diffusion of gases. He also extended the theory of probability and pioneered its application to the theory of gases. His contributions to mechanics were published between 1897 and 1904. At a later age Boltzmann became more interested in philosophical questions, which led, one year before his death, to the publication of his "Populäre Schriften".

BERNARD JAFFE

BOND, CHEMICAL

The term "bond" or, more completely, the phrase "chemical bond" describes the existence of a force of union between two atoms or two groups of atoms that results in sufficient stability of the resultant aggregate to make it convenient for the chemist to consider the aggregate as an independent molecular species. From the chemical point of view, bonds are best described in terms of three extreme types: ionic bonds, covalent bonds, and metallic bonds. The forces that cause the bonding between atoms arise from the interactions between charged particles electrons (–) and nuclei (+), and the three extreme types representing limiting cases of the nature of the average distribution of electronic (negative) charge with respect to the relatively stationary (positive) nuclei.

The empirical description of a chemical bond may be made either chemically or physically. The chemical description embraces the reactions employed in the formation of the bond, the kinds of reactivity that the bond may or may not show, and the physical properties (solubility, melting point, volatility, electrical conductivity, etc.) of the compound that reflect the nature of the bonds that hold its atoms together. The physical description includes quantitative measures of the strength of the union and the symmetry or lack thereof of the electric charge distribution. Valence theory can be said to have as one of its ultimate goals the complete rationalization of the properties of bonds in terms of the quantum mechanical theory of matter.

The most commonly employed description of bonds and the binding of atoms is based on the picture due largely to Lewis and elaborated by Sidgwick, and Pauling, of the basic element of the bonding of atoms arising from the sharing of one or more pairs of electrons by the bonded atoms. If the bonding electron pair is largely held by one or the other of the atoms, the bond is *ionic*. If the electron pair is more or less equally shared by the bonded atoms, the bond is *covalent*. If in addition to being held more or less equally by the bonded atoms there is long range, easy mobility of the bonding (valence) electrons, the bond is *metallic*. All chemical substances can be ordered in a linear array in accordance with the nature of their bonds: at one extreme there are the substances with purely ionic bonds, e.g., the alkali metal halides. There exists an almost continuous series of substances in which the ionicity of the bonds decreases (aluminum chloride, cadmium chloride, etc.) until in the center of the linear array there is the prototype of substances with covalent bonds, diamond. The semiconductors form a class of substances with bonds that are intermediate between covalent and the other end of the array, the metals. It is to be noted that no sequence of substances can be listed that gives a direct transition from ionic binding to metallic binding. The description of bonds that are predominantly covalent usually includes two qualifications: (1), the bond order, that gives in multiples of two the number of electrons involved in the binding, and (2), the ionic character that indicates the dissymmetry of the electric charge distribution.

The strength of the unions of atoms, the bonds, may be quantitatively measured by bond energies, bond dissociation energies, bond force constants, and bond distances. Bond energies in other than diatomic molecules are hypothetical quantities defined by the postulate that the energy of atomization of a substance can be described as equal to the sum of the energies of the bonds broken in the atomization process. Although the postulate finds but scant theoretical justification, the concept of the bond energy as a constitutive molecular property has proved a powerful tool in the systematization of thermochemistry, particu-

larly when supplemented by the quantitative measure of ionic character of the bonds, the electronegativity differences of the atoms.

Bond dissociation energies, bond force constants, and bond distances are most succinctly described as parameters that characterize particular features of the hypersurface that relates the potential energy of a molecular system to the configuration of the atoms of which the system is comprised. These three quantities specify respectively the depth of the surface below an asymptote, the curvature of the surface, and the internuclear distances of the atoms at the potential energy minimum that corresponds to the equilibrium configuration of the atoms in the molecule. These three quantities are at least qualitatively interrelated. "Large" bond dissociation energies are invariably accompanied by "large" bond force constants and "short" bond distances, and conversely. Semiempirical relations of various ranges of validity and applicability between the three measures of bond strengths have been proposed. Like bond energies, bond distances constitute an approximately constitutive molecular property.

Bond energies and bond dissociation energies are determined from thermochemical data (energy of formation), reaction kinetic data (energy of activation), optical and mass spectrometric data. Bond force constants are computed from the spacing of vibrational energy levels under certain assumptions concerning the form of the potential energy as a function of molecular configuration. Bond distances are determined from the analysis of x ray, electron, and neutron diffraction patterns of molecules, and the spacing of rotational energy levels from infrared, Raman and microwave spectra.

The nature of the distribution of electric charge between bonded atoms is described by the bond dipole moment. There is no direct measure of the bond dipole moment in polyatomic molecules. Most of the estimates of the magnitudes of bond dipole moments have come from measurements of the permanent dipole moments of molecules (from the temperature dependence of the dielectric polarization or the difference between the dielectric polarization and the molecular refraction) by means of the assumption that the bond dipole moments add vectorially to give the molecular dipole moment. In recent years measurements of the Stark effect in microwave absorption spectroscopy have provided a precise means of determining the molecular dipole moment characteristic of a particular vibrational state of a molecule. This is in contrast to the average value obtained from dielectric measurements.

In conclusion it should be noted that the bond concept is typically a chemical concept and that a valence theory can be developed without recourse to this concept, i.e., molecular orbital theory.

D. P. STEVENSON

Cross-references: *Molecules, Atoms, Energy, Valence, Ions, Dissociation, Dipole Moment*

BORATES

The principal natural borates of commercial importance today and their sources are:

Name	Approx. Composition	Deposits
Tincal (Natural Borax)	$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$	U. S., Tibet
Kernite (Rasorite)	$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	U. S.
Colemanite	$2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	U. S.
Ulexite (Bornatracalcite)	$\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$	U. S., Chile, Argentina, Bolivia, Peru
Piceite (Pandermitite)	$5\text{CaO} \cdot 6\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	Turkey (Asia Minor)

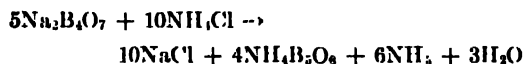
Five American firms reported production of boron compounds from natural sources in 1953: American Potash & Chemical Corp. recovered boron compounds from the brine of Searles Lake at Trona, Calif.; Columbia-Southern Chemical Corp. obtained borax in Inyo County, Calif.; Pacific Coast Borax Co. mined kernite at Death Valley Junction; United States Borax Co. obtained colemanite (hydrous calcium borate) from a vein deposit near Shoshone, Calif.; and West End Chemical Co. recovered boron compounds from the brine of Searles Lake. The water-soluble borates have been most studied. They are limited to the salts of alkali metals. From the systems $\text{M}_2\text{O} - \text{B}_2\text{O}_3 - \text{H}_2\text{O}$ the following salts separate at 30°C :

Metaborates	Tetraborates	Pentaborates
$\text{LiBO}_2 \cdot 8\text{H}_2\text{O}$	$\text{Li}_2\text{B}_4\text{O}_7 \cdot 7\text{H}_2\text{O}$	$\text{LiB}_5\text{O}_{10} \cdot 5\text{H}_2\text{O}$
$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	$\text{NaB}_5\text{O}_{10} \cdot 5\text{H}_2\text{O}$
$\text{KBO}_2 \cdot 2.5\text{H}_2\text{O}$	$\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	$\text{KB}_5\text{O}_{10} \cdot 4\text{H}_2\text{O}$

The borates react with strong aqueous acid to precipitate orthoboric acid.



The alkali metal borates in general react with the soluble salts of other metals to precipitate the heavy-metal borates. This reaction is partially responsible for the softening action of borates in hard water. The sodium borates react with aqueous ammonium chloride to precipitate ammonium pentaborate:



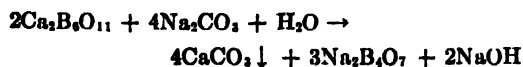
When heated to elevated temperatures, ammonium pentaborate decomposes to ammonia, boric oxide, and water.



Colemanite is commonly converted to boric acid by adding SO_2 or H_2SO_4 and floating the boric acid from the gangue.



Colemanite is converted to borax by boiling with soda ash, filtering from the calcium or magnesium carbonate, and allowing the borax to crystallize.

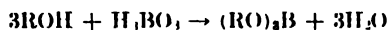


The transition metals form metaborates, often distinctively colored, upon fusion of their salts with borax; but the chemistry and structure of these compounds have apparently been little studied.

Scandium, yttrium, and indium borates are the only known orthoborates and have structures similar to those of CaCO_3 and NaNO_3 with planar BO_3 groups. The most unique factor in the structure of the borates is the tendency toward formation of the boroxin (B_3O_3) ring. For example, in the alkali-metal metaborates the anions are cyclic $(\text{BO}_2)_n$ trimers. However, in calcium metaborate the anions are linear $(\text{BO}_2)_n$ polymers. Both borax and colemanite have long chain anions containing boroxin rings. The pentaborate anion has two boroxin rings sharing a tetrahedrally coordinated boron.

Perborates. Sodium "perborate," obtained by the action of hydrogen peroxide and sodium hydroxide, or sodium peroxide, on cooled borax solution, formerly considered to be a perborate $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, is probably a borate containing hydrogen peroxide of crystallization, $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$. It does not liberate iodine from concentrated potassium iodide solution. The compound ("perborax") is stable in the dry state and only sparingly soluble in water. The solution has bleaching and antiseptic properties. It is stable at room temperature but evolves oxygen when heated. The solid loses $3\text{H}_2\text{O}$ at $50-55^\circ\text{C}$, and, if it is then heated in a vacuum at 120°C , it loses another molecule of water, leaving a yellow solid formulated as $(\text{NaBO}_2)_n \cdot \text{O}$, which evolves oxygen in contact with water, but does not liberate iodine from concentrated potassium iodide solution. The crystalline perborate $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ is also obtained by the electrolysis of a solution of borax and sodium carbonate with a platinum gauze anode.

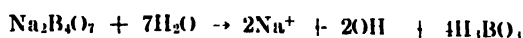
Organic Borates. The alkyl borates are prepared by refluxing the corresponding alcohol with boric acid or boric oxide. The water formed is removed by distillation as either the overhead or residual product, depending on the relative volatilities of the water and the alkyl borate,



The preceding reaction is readily reversed with the lower alkyl borates. The hydrolysis is slower with increasing alkyl chain length. The major present uses of alkyl borates are as volatile welding fluxes and as intermediates in the preparation of borohydrides. Both American Potash and Chemical Corp. and Pacific Coast Borax Co. are offering several alkyl borates for product development.

Analysis. Analysis of borates usually involves treatment of the substances with methanol and sulfuric acid. For qualitative analysis the methanol is ignited. A green flame indicates the presence of boron. For quantitative analysis, the mixture is distilled into water. Volatilization of the methyl borate removes it from interfering salts. It hydrolyzes readily in the water to boric acid. This is complexed with mannitol to form a strong monoprotic acid, which is titrated with standard base. The soluble borates hydrolyze com-

pletely enough to be titrated directly with standard acid for alkali metal content:



Uses. The enamel industry is the most important consumer of borates. Most enamels contain 25 to 40% borax. The glass industry is the second most important consumer, for use in borosilicate heat-resistant glasses. Other major uses are in glazing of chinaware, pottery, brick, and tile, as a softener for detergent mixtures, and in the production of the abrasive boron carbide.

ROY M. ADAMS

Cross-references: *Boron, Borides*

BORIDES

Several borides were prepared before 1900 and by 1935 some of the crystal structures had been determined. Recently, however, because of a growing interest in high temperature materials, the transition metal borides have been the subject of intensive study by L. Andrieux, L. Brewer, R. Kieffer, R. Kassling, J. T. Norton, P. Schwarzkopf, their co workers and many others.

The borides do not conform to the simple valency rules which determine the composition of many chemical compounds. The borides, as well as certain other interstitial compounds such as the carbides and nitrides of the transitional metals, defy interpretation in terms of any rational valency rules. Further examination shows that for many of the borides, the stoichiometric laws are no longer rigorously valid. Hence, the borides can be called compounds only in the sense that they exist as a solid phase of characteristic structure, which generally conforms closely to a simple chemical formula, but which may exist over a limited range of chemical composition. In view of this, the borides will logically be discussed in terms of their crystal structure. Although it is not yet possible to state the principles governing the boride structures, one feature is outstanding. This is the tendency for the boron atoms to be linked together to form zigzag chains, 2-dimensional nets or 3-dimensional frameworks extending throughout the whole crystal. The boron-boron bond plays a prominent part in the boride structures and their formulas are generally quite different from those of the interstitial carbides and nitrides. This linking together of the boron atoms seems to preclude the applicability of the Hagg rule. Consequently, there are no discontinuities in the properties of the borides when the critical ratio of the radius of the boron atom exceeds 0.59. The Hagg rule would appear to apply only when the metalloid atoms are in isolated positions in the lattice as in certain carbides and nitrides.

Borides may be obtained by sintering mixtures of the powdered metal with boron at temperatures of 1,800 to 2,000°C. The material thus obtained may be compacted and purified by further sintering compressed bars in a vacuum or low pressure inert atmosphere at temperatures near the melting point. Most of the impurities, being more volatile than the refractory borides, will be volatilized

away. Very pure boride samples have been prepared in this way.

Borides are also prepared by the thermite process in which a mixture of the metal oxide and boric oxide are reduced by Al, Mg, Si or C. The intermediate products react to form the boride. The boride crystals must then be separated from the by-products. This is difficult and usually results in impure products.

Several borides have been prepared by the electrolysis of fused salts. A molten mixture of the borate and fluoride of the metal is electrolyzed between graphite electrodes. The boride is deposited at the cathode and must be chemically separated from the mixture.

Borides have also been deposited from the vapor phase. A tungsten filament is heated in mixed vapors of boron tribromide, hydrogen, and a volatile metallic halide. The reaction, proceeding at the surface of the incandescent filament, deposits a coating of the boride. Large single boride crystals have been prepared in this way.

The borides are most remarkable for their thermal and chemical stability, hardness, and true metallic properties. The hardness of the borides lies in general between the diamond (Mohs 10) and the topaz (Mohs 8). The metallic character of the borides is evident from their low electrical resistivities and high thermal conductivities. The borides also have positive temperature coefficients of resistivity, showing that true metallic conduction is involved. Superconductivity has been reported for some of the borides. In several cases, however, these results have not been substantiated when very pure samples were examined. The borides are very refractory, with melting points in most cases between 2,000 and 3,000°C. The thermal stability of the diborides of the metals of Group IVa are exceptionally high. The borides are very stable chemically. They are not attacked by moisture or air at moderate temperatures and in nearly all cases do not react with HCl or HF. All the borides, however, are readily dissolved by molten alkali hydroxides. The transition metal diborides and all of the borides of Group VIa are stable at high temperatures in the presence of carbon or carbides.

The transitional metal borides are gray in color with a metallic luster. The alkaline earth borides are black and brownish black. The rare-earth borides are various shades of blue and purple. Lanthanum boride turns a deep red when moist. Thorium hexaboride is red and thorium tetraboride is yellow.

The Me_2B borides crystallize into structures which are isomorphous with CuAl_2 -type structure shown in Fig. 1. The small black spheres represent the boron atoms and the large white spheres represent the metal atoms. In this tetragonal structure there are four boron atoms and eight metal atoms in one unit cell. The boron atoms are arranged in layers with the metal atoms interleaved between them. Although the boron atoms lie in layers, they are apparently isolated with no boron-boron binding in these layers. However, each boron atom does have two close boron neighbors, directly above and below it in adjacent boron



FIG. 1

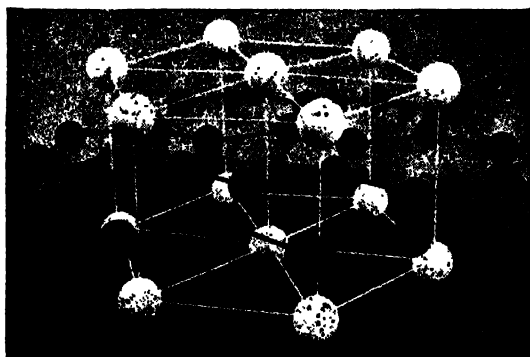


FIG. 2

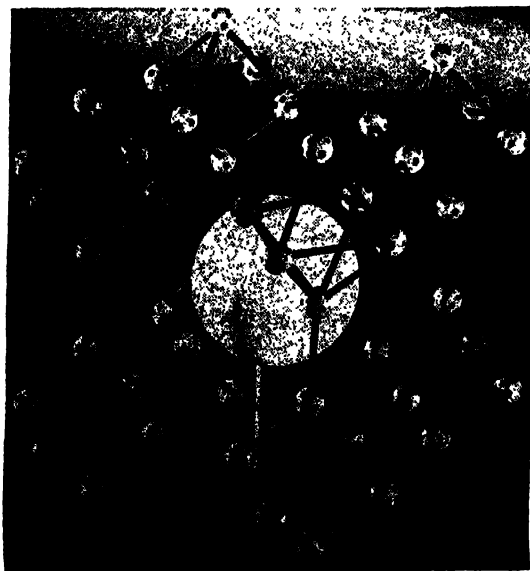


FIG. 3

planes. The metal atoms form pairs, as shown, and the distance between the atoms of such a pair is shorter than in the metal crystal. These pairs, one above the other and rotated 90° , form tetrahedra of metal atoms. The isolated boron atoms then fit in the holes between the tetrahedra.

The MeB_2 borides have a hexagonal AlB_2 -type structure as shown in Fig. 2. In this structure the arrangement again consists of alternate layers of boron atoms and metal atoms. The boron layer consists of hexagonal meshes like that of the graphite layer structure. Each boron atom is located at the center of a triangular prism of metal atoms. The metal atoms form a simple hexagonal structure. Each metal atom has twelve equidistant boron neighbors, six in the plane above it and six in the plane below. In the boron planes each atom is equidistant from three other boron atoms. Each boron atom has six equidistant metal atoms at the apexes of the triangular prism.

The alkaline-earth metals, the rare-earth metals and thorium all form hexaborides with the CaB_6 -type structure. This crystal structure is shown in Fig. 3. The small boron atoms form a three-dimensional framework structure which surrounds the large metal atoms. The boron framework is made up of octahedra, one at each corner of the cube. These are bonded together at their apexes. Each boron atom has four adjacent neighbors in its own octahedra and another neighbor in the direction of one of the cubical main axes.

The monoborides have at least two different crystal structures characterized by zigzag chains of boron atoms extending indefinitely throughout the crystal. Because of their low scattering powers for x-rays, the positions of the boron atoms are not always readily determined and frequently some doubt exists as to their exact locations in some of these structures. The compound ferric boride, FeB , has an orthorhombic crystal structure which is isomorphous with CoB . In this structure, each boron atom is surrounded by six iron atoms at the apexes of a trigonal prism. However, the nearest neighbors to each boron atom are two other boron atoms, thus forming an infinite boron zigzag chain. Several other monoborides form variations of this structure, some tetragonal, but all have boron chains.

The dodecaboride, ZrB_{12} , is isomorphous with UB_{12} . This structure consists of a three-dimensional framework of boron atoms with metal atoms located in the interstices of this skeleton. A face-centered cubic cell contains four ZrB_{12} units.

The AlB_{12} compound has three structures; a tetragonal diamond-like structure and graphitic structures of both tetragonal and monoclinic systems.

The tetraborides of Ce, Th and U form tetragonal structures with the metal atoms in sheets and the boron atoms in positions resembling both the diboride and hexaboride structures. With the intensive study now being devoted to refractory materials it is most likely that many more boride compounds will be reported in the near future.

The high-melting borides of the transition metals in Groups IVa and VIa are considered most promising as high-temperature materials for such

applications as turbine buckets and rocket nozzles.

Lanthanum hexaboride is used as a thermionic cathode material because of its metallic properties and high chemical and thermal stability.

Small quantities of boron are frequently added to steel in the form of borides for improving its ability to be hardened.

Excellent references to the literature on the transition metal borides may be found in Schwarzkopf and Kieffer's book "Refractory Hard Metals".

J. M. LAFFERTY

Cross-references: *Borates, Boron*

BORON AND COMPOUNDS

Boron, essentially metalloidal in character (in this respect differing from all the other, strictly metallic elements of Group III) is the fifth element of the periodic table, having an atomic weight of 10.82, with known isotopes of mass numbers 10 and 11. In the form of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), it has been an article of commerce for hundreds of years. The element itself is difficult of isolation, and many of the characteristics assigned to it by early investigators are now known to refer to highly impure and oxygen-containing material, and even to metallic borides and boro carbides, as made by reduction of oxygenated compounds. The element can be isolated, in pure form, by reducing boron trichloride or tribromide with hydrogen in a high-tension arc or by deposition on a heated tungsten wire, by dissociation of boron tribromide on a heated tungsten wire, by dissociation of diborane (B_2H_6), and, best from a production viewpoint, by electrolysis of potassium fluoborate (KBF_4) in fused potassium chloride, with or without boric oxide additions. The element, which appears in crystalline form from coarse to microcrystalline (so-called amorphous), has a density of 2.24–2.34, and its melting point is assumed in the 2000–2075°C range, although it may actually be nearer 2200°C. Its electrical conductivity is very low at room temperatures, but rises phenomenally with temperature; impurities have a great influence on the conductivity, carbon being extraordinarily effective even in 0.1% magnitude.

In alloy form, boron has proved of considerable worth in degassing and deoxidizing metals, copper-base in particular; similarly, boron aids in the grain refinement of aluminum. World War II brought boron steels rapidly to the fore, since quantities of the order of .0005 to .005% have proved adequate to increase hardenability very sharply. Here again, boron is usually added as a master alloy as ferroboron or as manganese-boron; the use of boron enables significant conservation of the scarcer ferro-alloying elements.

Boron has been suggested for motor-starting devices, thermal cut-outs for transformers, thermoelectric couples, pivot bearings, wire dies, and variable resistor devices. Fairly substantial amounts of boron are used as ignitors in rectifier and control tubes. The element is of value in atomic work because it occupies top rank of any

of the elements as a neutron absorber. Boron, when burned, gives highest BTU of any of the solid elements (25,120 BTU/lb) consequently is being seriously considered as a fuel booster in jet engines. Boron is a good reducing agent for many refractory oxides, and when its cost is lowered it could replace silicon and aluminum for this purpose. An important use for boron is in aluminum for making wire of high electrical conductivity. In certain other aluminum base alloys, it is used in minute amounts to confer exceptional strength, especially to those alloys which are sand cast, and require no heat treatment.

Elemental boron unites readily with all the halogens, but it is unaffected by boiling HCl or HF ; conversely, with HI it reacts explosively. Concentrated nitric acid or hot sulfuric acid reacts slowly on massive boron; caustic alkalis, either as aqueous solution or in fused form, have substantially no effect. Fused sodium peroxide or a fused mixture of sodium carbonate and potassium nitrate, on the other hand, react vigorously. In air, the massive element is unaffected at 750°C, and action is slow even at 1000°C; in oxygen, attack at 1000°C is quite rapid. Surprisingly, finely divided material, of 0.1–10.0 micron range size, oxidizes slowly even at room temperature; in general, the finely divided material is far more reactive than the massive.

The best known compounds of boron are derivatives of boric acid, H_3BO_3 , and its anhydride, B_2O_3 . Few simple salts are known derived from H_3BO_3 or the metaboric acid, HBO_2 ; most natural and synthetic salts are derived from polyboric acids of greater complexity; borax, for example, is derived from tetraboric acid, $\text{H}_2\text{B}_4\text{O}_7$, being found in nature as taborite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$) and as native borax. Other important minerals are colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, and ulexite ("cotton ball") $\text{NaCaB}_6\text{O}_{11} \cdot 8\text{H}_2\text{O}$.

A rare, but remarkable, compound of boron is the nitride, BN , a fine white powder with a hexagonal graphite like platelet structure. Of very low apparent density, significant oxidation resistance (up to about 650°C), very high melting point (about 3000°C), and extremely high electrical resistivity, the material has frequently been suggested as a special lubricant and for crucible purposes.

The hydrides of boron—in many structural respects resembling the hydrocarbons—have been receiving considerable attention recently, particularly along the lines of jet and rocket fuels. In contradistinction to the hydrocarbons, they have negative heats of formation, with consequent unusually high energy liberation on oxidation.

By far the largest commercial utilizations of boron are in the form of boric acid and the borates; one of the more important is for standard and special glasses—in particular, the borosilicate type of glass, such as "Pyrex", with its low coefficient of expansion and high chemical resistance. Related to this is the use of borax in enamel frits. Borax has also found extensive utilization in cleansers, detergents, and water-softening mixtures, and as a mild alkali in industries as diverse as leather treatment and photography.

Metallurgical and welding fluxes are generally boron-based, copper-base metal fluxes, using borax or boric acid a major component, while silver solder fluxes frequently contain fluoborates. The borate salts are being used as fire-retardants in lumber, textiles, and similar combustible materials. Because of the bacteriostatic and fungistatic action of boric acid, it has become a standard pharmaceutical item in external medical washes—for eyewashes in particular; in recent years, however, a growing realization of the systemic toxicity of boric acid has resulted in less promiscuous use. Both the borates and fluoborates are increasingly being found as constituents of electroplating baths.

Despite its toxicity for both plant and animal life when in larger quantities, traces of boron have been found essential to normal plant growth, and crop depletion of boron from the soil has necessitated the addition of this element during fertilization of many soils. There is some reason to believe the boron to be necessary in protein synthesis from the plant carbohydrates, but little is known beyond this conjecture. Inadequate boron usually shows itself as plant stunting; requirements vary greatly, from about 1 to about 300 milligrams per kilogram of plant dry substance; most plants appear to be in the 10-20 milligram range. The variable range—between plant-essential boron content of the soil on the one hand, and toxic concentrations on the other hand—is remarkably narrow, being, for both extremes, of the general order of a few milligrams of boron per kilogram of soil.

HUGH S. COOPER

Cross-references: *Borides, Borates*

BOYCE THOMPSON INSTITUTE

The Boyce Thompson Institute for Plant Research, Inc. was organized as a nonprofit, membership corporation under the laws of the State of New York on October 27, 1924. It was founded and endowed by William Boyce Thompson, financier and mining expert, to expand human knowledge and promote the welfare of mankind.

The general idea of a separate institution was first embodied in the Farm and Research Corporation organized in 1919. During the next five years, a plan for the present Institute evolved along lines proposed by Professor John M. Coulter of the University of Chicago. William Crocker was appointed Managing Director, a library of over 20,000 volumes was initiated, and the staff was organized.

The principal offices and laboratories are located on a 7-acre tract at 1086 N. Broadway in Yonkers, N. Y. about nineteen miles north of downtown New York City. There are 106,000 square feet of floor space in the major building and almost 30,000 square feet of greenhouses attached to it. The modernly equipped laboratories contain special facilities such as light-temperature control chambers, refrigerated rooms, Peet-Grady and other insect rearing and testing establishments, precision spray laboratories and temperature-

humidity cabinets for infesting plants with pathogens. Additional plant-growing facilities are available on a 19-acre experimental farm and a 210-acre arboretum where 3,000 species of plants are maintained for study.

The affairs of the Institute are managed through a Board of Directors whose members are appointed annually by the eleven Members of the Corporation who serve in the capacity of trustees and fill vacancies in their membership by election. The principal officers of the Corporation in 1951 were Chairman of the Board, Fred Searls, Jr.; Vice-Chairman of the Board, Mrs. Peggy Downey; Secretary, John M. Arthur; Treasurer, Wm. T. Smith; and Managing Director, George L. McNew. The latter, appointed upon retirement of Dr. Crocker on September 1, 1949, is the principal executive officer charged with the responsibility of actively managing the affairs of the Institute and organizing its research program under the general policies established by the Board of Directors.

A research staff of 66 technically trained people conduct investigations organized as some 45 projects. Plant physiologists, plant pathologists, entomologists, biochemists, organic chemists, physical chemists, morphologists and geneticists work as members of research teams where their skills can be blended to best advantage rather than as members of professional departments. The scientists are relieved of routine operation by service and maintenance staffs employing 100 people.

The Institute program derives its support from an endowment established by the Founder and later augmented by the generosity of his wife, so total assets are about sixteen million dollars. Income from these funds supports the basic research programs. The institute also accepts supplementary funds from industry, government and private agencies who have special problems to solve either by fundamental or applied research. The basic philosophy of the Institute is that practical problems can be solved most expeditiously by developing fundamental knowledge on the processes involved. Its staff is expected to acquire such basic facts and skills that it can be of substantial service to industry, agriculture and government in promoting the public welfare.

Some of the basic problems investigated by the Institute in the past 30 years are: physiological processes of seed during storage and germination, nature of growth and differentiation in plant tissues, effect of light quality and intensity on growth and flowering habits of plants, mechanism of action of fungicides, relationship of chemical structure to biological activity of organic compounds, nature of cell walls in plants and chemical properties of cellulose fibers, method of glycoside formation in plants, effect of polyploidy upon plant development, nature of virus diseases of plants, insecticidal ingredients of plants, synergistic action of chemicals on insecticides, bud dormancy and its regulation, the regulation of cell multiplication, growth and maturation by chemicals and effect of air pollution on plant health.

Additional details on this program can be found

in the 17 volumes of the "*Contributions from Boyce Thompson Institute*" (1925-1954) or the condensed report by William Crocker: "*Growth of Plants*", published by Reinhold Publishing Corp. of New York in 1948.

GEORGE L. McNEW

BRAGG, SIR WILLIAM HENRY (1862-1942)

Called "one of the most illustrious ornaments of physics" and "one of the best loved friends of all science", the founder of x-ray science and the elder in one of the most famous father-son teams of scientists in history, Sir William was born on July 2, 1862 at Wigton, Cumberland, England. He stands as an example of rich development in years in which the prime of youth has passed; for though, naturally, he was a successful student and an eminently successful teacher, it was not until 18 years after his departure from Cambridge to accept the professorship of mathematics and physics at the University of Adelaide, South Australia, that he published his first paper when he was more than 40 years old. It is very evident, however, that in the years which had preceded, there had been a great strengthening of mental forces to the point of readiness for service when once released in the search for new truth, for within three years of his first publication he had become a Fellow of the Royal Society, and from that time onward he was a continual contributor to the journals of science and the author of several great books.

Bragg's first paper on the range and ionization of alpha particles is one of the fundamental stepping stones in the science of radioactivity. In 1908 he returned to England as professor of physics at the University of Leeds, and it was not long before he became interested in x-ray research, coming into the field at a time when, with the principles of the quantum theory knocking at the doors of science, conventional electromagnetic views as to the behavior of nature held powerful sway. Bragg was a strong advocate of the particle nature of x rays, and his masterly writing invited considerable controversy with C. G. Barkla and others. It is characteristic of Bragg's broadness of view and his adaptability to changing pictures, that, following von Laue's fundamental discovery in 1912 of diffraction of x rays by crystals, he entered that field with enthusiasm and in collaboration with his son, William Lawrence Bragg, became the most prominent worker in the field which established the science of x ray spectroscopy.

The first spectrometer, still a prized possession of the University of Leeds, was built, and with it one of Bragg's young students, Moseley, performed the notable experiments which have immortalized his name. Bragg was at Leeds when the first World War broke out, but he became professor of Physics at University College, London, in 1915, though his time during the war was devoted to government service. He became Director of the Royal Institution and of the Davy-Faraday Research Laboratory in 1923, where he remained until his death on March 12, 1942. In this position

his powers reached their maximum field of usefulness. Endowed with all the personal charm so essential to the office, he was a worthy successor to Faraday, not only as a fruitful investigator, but as an inspiring speaker possessed of a gift for lucidity which made his lectures a joy, both to the man of science and to the layman. One of the most inspiring experiences of visitors to this kindly, courteous man, of whom the writer was one, was to have the original notes made by Faraday of Sir Humphry Davy's lectures at the Royal Institution displayed. Sir William was the recipient of many honors, including the Nobel Prize in 1915. He was respected and beloved all over the World for the greatness of his scientific ability and of his spirit, and for the simplicity of his manner. (Based in part on an obituary by W. F. G. Swann).

GEORGE L. CLARK

BREWING

Brewing is the production of beer and ale, a process involving a complex series of enzymatic reactions. Most important is the conversion of starch by the malt enzymes to a malt extract primarily composed of maltose (wort), which in turn is fermented with yeast of various types. The basic ingredient for both is malt, and United States Alcohol Tax Laws refer to both beer and ale as "alcoholic malt beverages" in contrast to wine, which is made from grapes.

Malt is the basic brewing material. It contributes most of the starch and all of the enzymes for the overall conversion during mashing. Many types of grain can be malted, but practically all malt used for brewing is barley malt. The primary purpose of malting is to activate the enzyme system in the barley. The process resembles the initial phase of the natural growth cycle for a kernel of grain. Barley is steeped in water to absorb moisture. Intermittent aeration promotes growth. The germination is carried out in drums or compartments with turning devices to prevent matting of the rootlets. The growth is controlled by passing moist air through the germinating barley. Progress of germination is followed by observing the length of the acrospire. Satisfactory modification is normally accomplished when the acrospire approaches the end of the kernel and is ready to protrude. At that stage the germinated "green" malt is transferred to malt kilns where the growth is arrested by hot air drying. Both aroma and enzymatic activity of the malt are greatly influenced by the moisture left in the malt when high heat is applied during the final kilning. In accordance with the American tendency to specialization, malting has become a separate industry.

Hops are the blossoms of the female hop vine. The brewing quality is identified with the resinous substances humulone and lupulone, located in small lemon-colored glands near the stem of each petal. They impart a bitter taste and pleasant aroma. Rice, corn grits and other cereals are used as extra sources of starch. Flavor-wise adjuncts serve as diluents to avoid the slightly satiating character of all malt beer. Water has played a

great role in brewing of fine beer. It still does; but with today's better understanding of brewing chemistry, it is normally possible to augment the natural minerals in water to meet specific requirements. All brewing water must, however, be clean and free of foreign taste or odor.

Brewing is a batch process throughout. In fact, the basic process steps have been essentially unaltered during the last 100 years. Progress with biological control and statistical quality control, together with automatic instrumentation, has made it possible to produce fine beer with great consistency.

The initial phase of the brewing process is production of wort. It entails milling, mashing, extraction and boiling with hops. Malt is crushed to expose the solids for thorough wetting, which must precede the enzymatic hydrolysis during mashing. The malt husks should be kept relatively intact, since they later serve as filter aids for the separation of wort from the undissolved solids. Malt mills are therefore constructed with several roller couples and intermediate screens. The starchy materials are squeezed out of the husks and the gritty particles are ground further.

Mashing is the preparation of a malt extract (wort) from malt and cereals by enzymatic hydrolysis. The primary products of mashing are maltose, dextrins and a small, but important, fraction of protein which is essential for good foam and smoothness of the finished beer. In addition, wort must contain the necessary nutrients for yeast growth. Mashing involves a complex interplay of chemical and enzymatic reactions which are not fully understood. The primary reaction is enzymatic decomposition of starch by alpha and beta-amylase. Their action is synergistic: the starch molecule is a glucose polymer with branched chain structure. Alpha-amylase splits off dimer-units of maltose from the straight chains while beta-amylase splits off chain sections, thus exposing more straight chain terminals for the action of alpha-amylase. There is evidence of a third enzyme, limit dextrinase, which decomposes thermal sections of dextrins which cannot be attacked by alpha- or beta-amylase. Many other enzymes play a role in mashing. Some enzymatic reactions precede and condition the mash for the primary conversion of starch, while other reactions such as the hydrolysis of malt protein largely runs concurrent to the starch conversion. All the enzymatic reactions in the mash are influenced by temperature, pH, concentration and process time, but not to the same extent. A certain ratio of fermentable sugar to nonfermentable sugar can therefore be obtained in different ways and with varying side reactions. The art of brewing entails the empirical experience of choosing the best procedure for getting the most desirable side reactions along with the major conversion of maltose and dextrin.

Lautering is the separation of solubilized extract, wort, from the grain residue. Plate and frame filters and special lauter tuns are used. The latter are gravity filters with rotating knives to plow up the grain bed and prevent it from packing tight

during filtration. Malt husks serve as filter aids while the filter cloth or strainer bottoms merely act as supports for the grains. Separation of the original wort is followed by sparging with hot water to remove the last wort from the grains. The concentration of the first wort is about 18-20% extract to produce a finished wort with 12.5% extract.

For flavoring, the brew is boiled with hops. At the same time, the combined action of boiling, low pH, and hops, renders the brew sterile. Vigorous boiling promotes coagulation of unstable proteins and is beneficial for the ultimate beer stability. The process of coagulation and separation of unstable materials continues through all the subsequent processing.

Wort Cooling requires a high degree of sanitation, for the cooled wort provides an excellent substrate for competitive organisms. The brew is therefore vulnerable to spoilage until pitched with yeast and in vigorous fermentation.

Fermentation. Fermentation is the key operation in brewing and is conducted with great care. Both the type of yeast and the entire scheme of fermentation is reflected in the taste and aroma of the finished product. Air is essential for the initial propagation of yeast, though the fermentation itself is an anaerobic process. The fermentable sugars are split to ethyl alcohol and carbon dioxide by enzymatic action of the fermenting yeast. Temperature greatly influences the velocity of fermentation as well as the taste and aroma probably through formation of fermentation by products.

Brewery yeasts are pure cultures of the species *Saccharomyces cerevisia*. All multiplication is by cell division. With a high degree of sanitation and careful handling, it is possible to use the same yeast for many successive fermentations. Ale yeast is "top-fermenting", meaning that the yeast cells agglutinate during fermentation and rise to the surface with the ascending (CO₂) bubbles. Beer yeast is often called "lager yeast." It is "bottom fermenting". The yeast cells stay suspended in the fermenting beer and settle to the bottom at the end of fermentation.

Freshly fermented beer is harsh tasting and must be matured by aging. The flavor modification can be ascertained organoleptically, but the chemical reactions involved are obscure and probably involve trace constituents such as aldehydes or mercaptans. Aging also entails clarification and carbonation of the beer. Two methods of carbonation are used in the American brewing industry: after-fermentation and induced carbonation. Fine beers are produced by both methods.

Beer is not a true solution. The proteins important to foam and smoothness are colloids and inherently are prone to coagulate and form haze in the finished beer. Beer is shipped long distances and is not always consumed right away. This led American brewers to perfect the technique of eliminating the protein fractions most prone to precipitate. Both solubilization and precipitation methods are used and often in conjunction. The solubilization method is called "chillproofing"

and involves addition of proteolytic enzymes to the beer. Proteolysis is not selective; the enzymes will attack both stable and unstable proteins. Precipitation by adsorption to mineral gels such as bentonite is more selective, but requires more precision in processing. Chemical precipitants such as tannin are also used.

Beer is clarified by filtration to remove suspended proteinaceous material. Two or more successive filtrations permit rational selection of the best filter aids. Diatomaceous filters are well-suited for the first filtrate. The filter surface is kept from clogging by continuous addition of diatomaceous earth which imbeds the retained solids. The second filtration is often done on "pulp" filters with fixed filter pads of cotton fibers. There are many variations and combinations of filtration. Public demand for brilliant clear beer has spurred great progress in the filtration technique. High brilliancy is conducive to good stability since suspended solids tend to act as foci for precipitation and produce a "snow balling" effect.

The brewing industry in the United States produces a total of 80-90 million barrels of 31 gallons each annually and pays nearly one billion dollars in taxes. There are almost 300 breweries operating in the United States. The industry is represented by United States Brewers Foundation and Brewers Association of America. The brewing profession has two technical societies, Master Brewers Association of America, The American Society of Brewing Chemists and the Brewing Industries Research Institute.

EDWARD W. HUBER AND ERIK KRABBE

Cross-references: *American Institute of Baking, Enzymes, Bacteriology, Yeast*

BREWING INDUSTRIES RESEARCH INSTITUTE

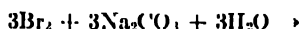
The object of Brewing Industries Research Institute is to sponsor research for the benefit of the brewing industry as a whole and to publish the findings thereof. Specifically, the purpose is to carry out important basic research which, by nature, is unlikely to be solved by the individual members of the industry. The Institute was founded January 9, 1952 and registered as a non-profit corporation in the State of Illinois. Official address is The Rookery, 209 South LaSalle Street, Chicago 4, Illinois. First and present president is Mr. Edward W. Huber. Charter members of Brewing Industries Research Institute were the professional and industrial organizations of the brewing industry as listed below: (1) American Society of Brewing Chemists (2) Barley and Malt Institute (3) Master Brewers Association of America (4) Small Brewers Association of America (5) United States Brewers Foundation, Inc. The activity of B. I. R. I. has been the sponsoring of research programs in universities and research institutions. Major projects pertain to the brewing ingredients and beer itself. Several short range projects have been successfully completed.

ERIK KRABBE AND EDWARD W. HUBER

BROMATES

Bromates are salts of the very unstable acid HBrO_3 (bromic acid), which exists only in aqueous solutions. The salts, though quite stable at ordinary temperature when dry or in neutral or alkaline aqueous solution, are strong oxidizing agents in acid solution. Like the chlorates, they react vigorously with organic matter when heated or subjected to shock.

Alkali bromates are prepared by the electrolytic oxidation of bromides or by the reaction of bromine with an alkali hydroxide or carbonate, in water:



The bromates are generally less soluble than the bromides and may be crystallized from the mixture.

Uses for the bromates are based upon their oxidizing properties. The baking characteristics of wheat flour are improved by addition of 5 to 10 parts of bromate per million; apparently the salt oxidizes sulfhydryl groups in the protein, which otherwise would affect the dough viscosity adversely. Bromates are also used as analytical reagents and in some hair wave preparations. "Mining salts" or "bromine salts" are mixtures of bromates with bromides, which yield bromine upon acidification and have some uses as brominating agents.

V. A. STENGER

BROMIDES

Inorganic bromides are salts of hydrobromic acid, HBr . Their properties are intermediate between those of the chlorides and the iodides. Most metallic bromides are quite water-soluble, those of silver, lead and monovalent mercury, thallium or gold being exceptions. In the absence of chloride and iodide, a bromide can be detected and determined either volumetrically or gravimetrically by precipitation as silver bromide. Interference from iodide is avoided by first boiling with nitrous acid (sodium nitrite plus dilute sulfuric acid), whereby iodine is expelled. Bromide in the presence of chloride may be detected by oxidation to bromine (amber color) with chlorine water. It may also be determined by oxidation to bromate with sodium or potassium hypochlorite. The excess hypochlorite is decomposed with sodium formate and the bromate is determined by treatment with potassium iodide in acid solution, followed by titration of the liberated iodine.

Alkali and alkaline earth bromides are prepared most simply by treating the corresponding hydroxides or carbonates with hydrobromic acid, followed by evaporation and crystallization. Sodium and potassium bromides may also be recovered from mother liquors obtained in the preparation of bromates from the carbonates and

bromine. The major use for these compounds is in photography, in the preparation of the light-sensitive silver bromide emulsion. However, considerable quantities are also used in pharmacy, as mild sedatives. Bromides such as those of lithium and calcium, being very hygroscopic, find uses in air drying and refrigeration. Anhydrous aluminum and iron bromides are useful as catalysts of the Friedel Crafts type.

Hydrogen bromide, a corrosive, irritating gas, is prepared by burning bromine vapor with hydrogen. It dissolves readily in water, forming hydrobromic acid. Either the acid or the gas can be used in the preparation of various inorganic and organic bromides.

Of the organic bromides, ethylene dibromide has by far the greatest commercial use. As an ingredient of antiknock fluid for motor fuels it serves to react with tetraethyl lead, aiding in the removal of lead from the cylinders. Both methyl bromide and ethylene dibromide are employed widely as agricultural chemicals, for the sterilization of soils and the fumigation of grains and other food products. A number of organic bromides are used as intermediates in the synthesis of pharmaceuticals and other products. In general the introduction of bromine into a molecule increases its reactivity and density but decreases its volatility and flammability. Methylene chlorobromide and several other substituted bromomethanes are excellent fire extinguishers. Acetylene tetrabromide and other bromocompounds are used as heavy liquids for gauges, mineral separations, etc. Several brominated phenolic compounds are used as antiseptics or fungicides. Most of the organic bromides are toxic; inhalation of the vapors and contact with the liquids or solids should be avoided.

V. A. STENGER

Cross-references: *Antiknock Agents*

BROMINE

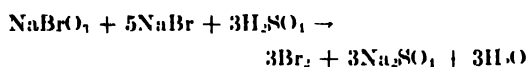
Bromine is a nonmetallic element of the halogen family, with chemical properties resembling those of chlorine and iodine (Group VII of Periodic System). At ordinary temperature it is a dark red-brown liquid which vaporizes readily. Both liquid and vapor are very corrosive and the vapor has an intensely irritating odor. The element has atomic number 35, and consists of two stable isotopes, Br^{79} and Br^{81} , present in nearly equal amounts so that the atomic weight is 79.916. The liquid and vapor are diatomic over a wide range of temperature.

It was discovered independently by A. J. Balard in France and C. Löwig in Germany, in 1825. Balard obtained it by chlorinating sea water bitterns and liberating the element by distillation, whereas Löwig treated salt spring brine with chlorine and extracted the bromine with ether. Balard selected the name from the Greek *Bromos*, meaning "stench".

Occurrence. The occurrence of bromine generally parallels that of chlorine. In the earth's crust, the latter is about 300 times as abundant as the

former. Neither element occurs free in nature, but is always found as a halide. With the exception of some rather rare silver salts, no natural mineral contains bromine as an essential constituent. Alkali and alkaline earth halides, because of their solubility, are susceptible to leaching from rocks and soils by rain water and are carried to the ocean where they accumulate. Average ocean water contains 67 mg of bromine per liter. In various parts of the world there are salt deposits or brines where bromine has been enriched by evaporation of water from prehistoric seas or salt lakes. Bromine is extracted commercially from the ocean, from underground brines in Michigan, Ohio and West Virginia (0.05 to 0.30% Br), from saline basins such as Searles Lake, California (0.085%) and the Dead Sea, Palestine (0.56%), and from solid salt beds at Stassfurt, Germany. In the latter, bromine is present in the form of chlorobromide mixed crystals with the more soluble components (carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and tachhydrite, $2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$).

Preparation. Bromine is prepared in the laboratory by reaction of a bromate with a bromide and acid, in water:

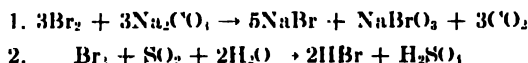


The bromine is distilled out and condensed together with a little water, from which it may be separated by gravity, and is dried by treatment with anhydrous calcium sulfate.

Commercially, bromide containing brines are treated with chlorine and the bromine is swept out by steam:



The mixture of steam, bromine, and some chlorine is condensed and the halogen layer is fractionally distilled to obtain pure bromine. In the recovery of bromine from ocean water the use of steam is not economically practical, so the bromine is blown out with air. The halogens are removed from the air stream either by scrubbing with sodium carbonate solution or by introducing sulfur dioxide and scrubbing with water:



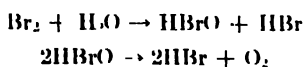
In the former case, bromine is regenerated by acidification as in the laboratory preparation above, whereas in the latter case, the acid mixture is rechlorinated and distilled as in the steam process. The waste sulfuric acid is used for acidifying the incoming ocean water, which must be brought to a pH below 4 before treatment with chlorine.

Properties. Bromine freezes at -7.2°C and boils at 58.8°C . The density of the liquid at 25°C is 3.104 and the specific heat is 0.107 calorie per gram. Heats of fusion and vaporization are 18.1 and 44.8 calories per gram, respectively. The solubility of bromine in water at 25°C is 3.35 grams per 100 grams of solution. In the presence of alkali halides, particularly potassium bromide, the solubility is increased. Presumably a complex polyhalide (KBr_3) is formed. Bromine is com-

pletely miscible with many of the common organic solvents such as carbon tetrachloride and benzene, though in most cases bromination occurs and the solutions are not stable.

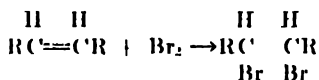
In reactivity bromine is similar to chlorine, though its normal oxidation potential is somewhat lower (-1.087 volts for the aqueous system $\text{Br}_2 + 2e \rightarrow 2\text{Br}^-$). Bromine attacks most metals. Aluminum reacts with it vigorously, with emission of light, and potassium reacts explosively. On the other hand, lead, nickel, and magnesium are not attacked and may be used as containers for the liquid. Even sodium does not react with dry bromine below 300°C . Iron and zinc are corroded rapidly if moisture is present.

Bromine hydrolyzes slightly in aqueous solution, producing hypobromous acid which is unstable:

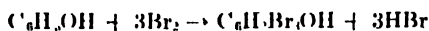


The liberated oxygen is responsible for the bleaching action of bromine water. Hypobromite solutions formed by neutralizing bromine water with alkali are also strong oxidants, capable of oxidizing ammonia to nitrogen, sulfur compounds to sulfates, and various metals to their higher valences. The hypobromite is also unstable, disproportionating to bromate and bromide.

Unsaturated organic compounds form *addition* products with bromine, in some cases almost quantitatively



The *substitution* reaction of phenol with bromine is also practically quantitative:



Uses. Most of the bromine that is produced is converted to ethylene dibromide (see **Bromides**). A small proportion is sold as liquid bromine for use in organic syntheses, as an analytical reagent, and for miscellaneous oxidizing purposes. Bromine is an effective antiseptic but except in specialized cases cannot compete economically with chlorine for water sterilization. The usefulness of bromine in synthesis stems from the ease with which it may be introduced and replaced in organic compounds. Since bromine may be replaced more readily than chlorine, the reaction conditions are frequently less drastic. Selective reactions are also possible so that, for example, two different groups may be introduced into a molecule by successive operations upon a bromochloro intermediate. Bromine also modifies the shades and solubilities of indigos and other colored compounds, thereby finding uses in the dye industry.

V. A. STENGER

Cross-references: *Bromates, Bromides, Dyeing*

BROWNIAN MOTION

In 1827 the British botanist, Robert Brown, discovered that extremely small particles suspended

in a liquid perform a chaotic zigzag movement, seemingly never ceasing and uninfluenced by any factor outside the system. This movement is now known as *Brownian molecular motion*. Robert Brown was born in 1773 at Montrose and died in 1858 in London. In 1787 he entered Marischal College in Aberdeen but two years later he moved to Edinburgh University. In 1801, as a naturalist, he undertook a trip to survey the almost unknown coasts of Australia. He returned to England in 1805 and was almost immediately appointed Librarian of the Linnaean Society. In 1827 Brown became Keeper of the new Botanical Department of the British Museum in London, an office he held until his death on June 10, 1858.

A liquid at rest, such as water in a glass, appears to be homogeneous, continuous and motionless throughout. If a powder consisting of extremely fine particles is mixed with the water and this mixture is stirred well, again no motion is noticeable after the dispersion has come to rest. Microscopic studies have revealed, however, that this is actually not the case and that the fine particles which have been placed in water, or any other fluid, will not sink if they are of colloidal size, but are endowed with a very vigorous motion which is quite haphazard and irregular. The particles, even though of colloidal dimensions, reflect enough light to be detectable in an ultramicroscope.

In 1863 C. Wiener said: "The movement does not originate in the particles themselves, nor in any cause exterior to the liquid, but must be attributed to internal movements characteristic of the fluid state." He also expressed the opinion that, according to thermokinetics, the movement of the dispersed particles is due to the irregular bombardment they receive from the surrounding molecules of the dispersion medium. His purely theoretical deductions were supported by a large number of very carefully conducted experiments carried out by Gouy and Cantoni.

Somewhat later, M. von Smoluchowski worked out the theory of the Brownian motion from a molecular kinetic point of view. According to him, the middle kinetic energy of a particle, which is moved about by the impact of the surrounding molecules of the liquid, must in stationary condition be equal to the kinetic energy of these molecules. Therefore, the particle must behave as if it were a molecule of a dissolved substance. A similar deduction was drawn by A. Einstein, who assumed that particles which can be made visible in a microscope and which show Brownian motion will exert on an impermeable membrane exactly the same osmotic pressure as an identical number of molecules would.

Brownian motion is characteristic of the particles in rubber latex and similar colloidal suspensions.

ERNST A. HAUSER

Cross-references: *Colloid Chemistry*

BUFFERS

When acid is added to an aqueous solution, the pH falls; when alkali is added, it rises. If the orig-

inal solution contains only typical salts without acidic or basic properties, this rise or fall may be very great. There are, however, many other solutions which can receive such additions with only a slight change in pH. The solutes responsible for this resistance to change in pH, or the solutions themselves, are known as *buffers*. A weak acid becomes a buffer when alkali is added, and a weak base becomes a buffer on the addition of acid. A simple buffer may be defined, in Bronsted's terminology, as a solution containing both a weak acid and its conjugate weak base. Buffer action is explained by the mobile equilibrium of a reversible reaction:



in which the base B is formed by the loss of a proton from the corresponding acid A. The acid may be a cation such as NH_4^+ , a neutral molecule such as CH_3COOH , or an anion such as $H_2PO_4^-$. When alkali is added, hydrogen ions are removed to form water; but, as long as the added alkali is not in excess of the buffer acid, many of the hydrogen ions are replaced by further ionization of A to maintain the equilibrium. When acid is added, this reaction is reversed as hydrogen ions combine with B to form A.

The pH of a buffer solution may be calculated by the mass law equation

$$pH = pK' + \log \frac{C_B}{C_A}$$

in which pK' is the negative logarithm of the apparent ionization constant of the buffer acid and the concentrations are those of the buffer base and its conjugate acid.

A striking illustration of effective buffer action may be found in a comparison of an unbuffered solution such as 0.1 M NaCl with a neutral phosphate buffer. In the former case, 0.01 mole of HCl will change the pH of 1 liter from 7.0 to 2.0, while 0.01 mole of NaOH will change it from 7.0 to 12.0. In the latter case, if 1 liter contains 0.06 mole of Na_2HPO_4 and 0.04 mole of NaH_2PO_4 , the initial pH is given by the equation:

$$pH = 6.80 + \log \frac{0.06}{0.04} = 6.80 + 0.18 = 6.98.$$

After the addition of 0.01 mole of HCl the equation becomes:

$$pH = 6.80 + \log \frac{0.05}{0.05} = 6.80$$

while after the addition of 0.01 mole of NaOH it is

$$pH = 6.80 + \log \frac{0.07}{0.03} = 6.80 + 0.37 = 7.17$$

The buffer has reduced the change in pH from ± 5.0 to less than ± 0.2 .

Fig. 1 shows how the pH of a buffer varies with the fraction of the buffer in its more basic form. The buffer value is greatest where the slope of the curve is least. This is true at the mid-point, where $C_A = C_B$ and $pH = pK'$. The slope is practically

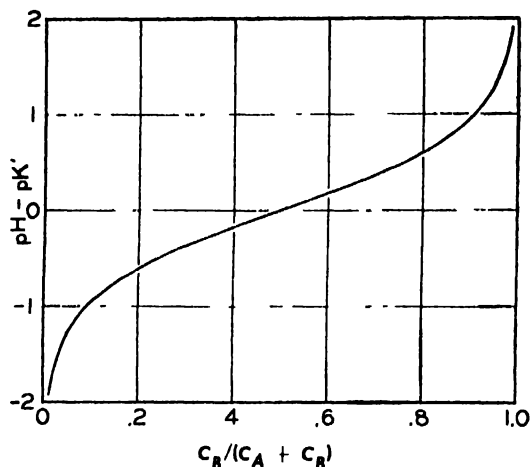


Fig. 1. pH of a simple buffer solution. Abscissas represent the fraction of the buffer in its more basic form. Ordinates are the difference between pH and pK' .

the same within a range of 0.5 pH unit above and below this point, but the buffer value is slight at pH values more than 1 unit greater or less than pK' . The curve of Fig. 1 has nearly the same shape as the titration curve of a buffer acid with NaOH or the titration curve of a buffer base with HCl. Sometimes buffers are prepared by such partial titrations, instead of by mixing a weak acid or base with one of its salts. Certain "universal" buffers, consisting of mixed acids partly neutralized by NaOH, have titration curves which are straight over a much wider pH interval. This is also true of the titration curves of some polybasic acids, such as citric acid, with several pK' values not more than 1 or 2 units apart. Other polybasic acids, such as phosphoric acid, with pK' values farther apart, yield curves having several sections, each somewhat similar to the graph in Fig. 1. At any pH the buffer value is proportional to the concentration of the effective buffer substances or groups.

The following table gives approximate pK' values, obtained from data in the literature, for several buffer systems:

Constituents	pK'
$H_2PO_4^-$, KH_2PO_4	2.1
$HCOOH$, $HCOONa$	3.6
CH_3COOH , CH_3COONa	4.6
KH_2PO_4 , Na_2HPO_4	6.8
HCl , $(CH_2OH)_3CNH_2$	8.1
$Na_2B_4O_7$, HCl or $NaOH$	9.2
NH_4Cl , NH_3	9.2
$NaHCO_3$, Na_2CO_3	10.0
Na_2HPO_4 , $NaOH$	11.6

Buffer substances which occur in nature include phosphates, carbonates and ammonium salts in the earth, proteins of plant and animal tissues, and the carbonic acid-bicarbonate system in blood.

Buffer action is especially important in biochemistry and analytical chemistry, as well as in many large-scale processes of applied chemistry. Ex-

amples of the latter include the manufacture of leather and of photographic materials, electroplating, sewage disposal and scientific agriculture.

DAVID I. HITCHCOCK

Cross-references: *Blood, Biochemistry, pH Acids, Bases*

BUNSEN, ROBERT WILHELM (1811-1899)

Robert Wilhelm Bunsen was born March 31, 1811 in Göttingen, Germany. As a boy he showed great interest in geology, but as a student at the University of Göttingen he devoted himself principally to chemistry, physics, mineralogy, and mathematics. In 1831 he obtained his doctorate from the University of Göttingen with a dissertation in the field of physics. The following year he won a travel stipend, of which he made the fullest use.

Back in Göttingen, he became a *Privatdozent* in the field of chemistry; here he discovered an antidote for arsenical poisoning, noteworthy because it represented one of Bunsen's few excursions into organic chemistry. When in 1835 his former teacher, Friedrich Stromeyer, died, he was invited to conduct Stromeyer's lectures on theoretical and practical chemistry. In 1836 he was appointed teacher at the Polytechnic School in Kassel.

From 1837 to 1842 he investigated blast-furnace processes. He found that almost half of the fuel produced heat was lost, and he demonstrated that this waste could easily be avoided. Upon the invitation of the British Association for the Advancement of Science, he investigated jointly with Lyon Playfair the conditions of British furnaces; he found the waste of heat to be even greater. These investigations resulted in the elaboration of his famous methods of measuring gaseous volumes, published in his book "*Gasometrische Methoden*" (1857).

Simultaneously he was occupied with practical experiments in producing galvanic current; he succeeded in replacing the expensive platinum of Grove's cells by carbon produced by him artificially. These Bunsen electrolytic cells were used extensively in industry at that time.

After almost 13 years' activity at Marburg, Bunsen accepted the Professorship of Chemistry at the University of Breslau (1851). A year later he went to the University of Heidelberg, succeeding Leopold Gmelin. In 1855 Bunsen moved into the university's new chemical laboratory, then considered the best equipped and largest German university laboratory. Bunsen's laboratory attracted chemists from all over the world, many remaining only a short time to qualify as "students of Bunsen's." Though organic chemistry became increasingly the most popular field of chemistry in the 1860's and 1870's, Bunsen refused to change his allegiance from his chosen area of inorganic chemistry.

Bunsen's achievements in Heidelberg were extensive. Besides devising the famous Bunsen burner, he discovered a method of separating metals by means of electric current. He produced

pure chrome and manganese from chloride solutions; light metals in large quantities through electric decomposition of their molten chlorides: magnesium, aluminum, sodium, barium, calcium, and lithium. Perhaps it was the dazzling white light generated when magnesium was burned which led Bunsen to a series of photochemical investigations made jointly with Henry E. Roscoe (1855-1862). In this connection he invented the grease spot photometer. In the years following, Bunsen continued his studies of light. In 1860, in collaboration with Gustav Kirchhoff, he published an epoch-making paper entitled *Chemische Analyse durch Spectralbeobachtungen*. With prophetic insight Bunsen predicted that spectrum analysis was destined to discover new elements. This was borne out in the case of rubidium and cesium, two new elements which he discovered the following year in the Durkheim saline waters.

In 1853 Bunsen published a general method of volumetric analysis, a method so well known today that few remember its originator, and established standard methods of analysis for silicates, ashes, and nitrogen in organic bodies. His last three investigations (1883-1885) dealt with the condensation of carbon dioxide on smooth glass surfaces and with capillary gas absorption generally. In 1887 Bunsen described a vapor calorimeter with which he determined the specific heat of platinum, glass, and water.

EUGENE MUELLER

BURTON, WILLIAM MERIAM (1865-19—)

Famous as the inventor of the first commercial process for cracking heavy petroleum oils into gasoline, Burton was the son of a Cleveland physician and attended Western Reserve University. There his interest was stimulated by Ira Remsen's textbook on organic chemistry. He decided to do graduate work under Remsen at Johns Hopkins, and to become a teacher.

While he was at Johns Hopkins, an uncle sent him a sample of "sour" petroleum from the Lima, Ohio, field. Burton experimented with this material and found that much of the objectionable sulfur could be removed with copper oxide. He applied for a patent, but learned that the process had already been patented by Herman Frasch. This work turned his interests definitely toward industry. Upon receiving his Ph.D. degree, in 1890, he was offered a job by the Standard Oil Company. Somewhat against the advice of Remsen, who considered an industrial career contrary to the learned tradition, he accepted. After a short period in Cleveland working with Frasch, he was sent to Standard of Indiana's new refinery at Whiting, Indiana. There he converted the second floor of an old farmhouse into one of the industry's first laboratories.

By 1900 he had become general manager of manufacturing. Automobiles were increasing rapidly in number, and Burton saw that it would be highly desirable to get more gasoline from each barrel of crude. Only about 20% could be obtained by simple distillation. Of particular interest as a

possible raw material was "gas oil," the fraction heavier than kerosene but lighter than lube oil. It had no major use.

Under the guidance of Dr. Burton and the specific direction of Dr. Robert E. Humphreys, the research staff tried to break up the large gas oil and other molecules by various methods of heating. They finally resorted to pressure to hold the gas oil as a liquid in the still until cracking temperatures were reached. Little was known about hydrocarbon behavior under such conditions, and there was some fear of detonation. There was also trouble with coke, which deposited on the bottom of the still as cracking progressed. At a temperature of about 720°F and a pressure of 75 psi, it was found possible to obtain considerable yields of gasoline. The coke problem was greatly reduced through the use of false bottom plates, devised by Dr. Humphreys. The parent Standard Oil Company considered the process too dangerous, and refused Burton's request for funds to build commercial units. Standard of Indiana became independent in 1911, however, and Burton became a director of the company. He persuaded the board to install 120 cracking stills. The process proved highly successful. Its effects, both direct and indirect, were far-reaching. By doubling the yield of gasoline obtainable from crude, it conserved petroleum reserves; at the same time it insured the future of the gasoline automobile. Patents covering the process were later appraised as among the most valuable ever issued. The company licensed them widely, and thus set the example for a general oil industry practice of licensing patented developments on reasonable terms.

The success of Burton's efforts stimulated other research. In addition, the required heat and pressure created many technical problems. Solution of them led to a whole new science of refinery engineering. Because cracked gasoline turned out to have better antiknock properties than straight-run gasoline, it pointed the way to other types of tailor-made molecules. The by-product gases resulting from cracking were rich in olefins. These served as raw materials for a host of chemical products: alcohols, glycols, plastics, organic acids, synthetic rubber, and synthetic fibers.

Dr. Burton became president of the Standard Oil Company in 1918. He retired in 1927. His achievements have been recognized by a number of scientific awards: the Willard Gibbs Medal of the Chicago Section, American Chemical Society, in 1918; the Perkin Medal of the Society of Chemical Industry, in 1921; and the American Petroleum Institute Gold Medal for Distinguished Achievement, in 1947.

ROBERT E. WILSON

Cross-references: *Cracking, Gasoline*

BUTADIENE

The term "butadiene" is applied to those four-carbon straight-chain hydrocarbons containing two carbon-carbon double bonds. In 1,2-butadiene these linkages are between adjacent car-

bon atoms, as shown by the structural formula $\text{CH}_2=\text{C}=\text{CH}-\text{CH}_3$. In the more common isomer, 1,3-butadiene they are separated by a single bond, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$. It is thus a *conjugated diene*, which is the basis of its great reactivity and tremendous commercial importance in the fields of synthetic rubber, plastics, drying oils, etc.

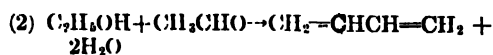
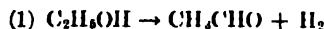
At atmospheric pressure and temperatures, 1,3-butadiene is a heavy, colorless gas, sp. gr. 1.921, with a characteristic odor. It may be condensed to a liquid, density 0.6504 gram per ml at its boiling point of -4.15°C . Toxicity of the vapors is of a relatively low order. The liquid freezes to a crystalline solid at -164.0°C .

1,3-Butadiene is found in gases resulting from high temperature decomposition of hydrocarbons and has been commercially recovered from the products of heavy oil cracking. It is also formed in cracking of ethane, propane, and butane, and of cyclics, particularly cyclohexene. Catalytic dehydrogenation of butane or butylene is an important source, as has been conversion of ethyl alcohol. In Germany, acetylene served as the primary source of butadiene.

In the United States, manufacture of 1,3-butadiene has been most economic by dehydrogenation of butane and butylene. During World War II, in 1942-43, a huge butadiene industry was built by the Federal Government, founded on these processes. Approximately 150,000 short tons of annual capacity was installed based on dehydrogenation of refinery cracking by-product butylenes over alkaline chromic oxide-iron oxide catalyst at about 1200°F. Another 80,000 short tons was based directly on dehydrogenation of the primary natural gas hydrocarbon *n*-butane, either in a two-stage process in which the first step is dehydrogenation to butylenes over a chromia-alumina catalyst at 1100-1150°F, or in a single stage to a mixture of butadiene and butylene over a similar catalyst.

Cracking of heavy oils, especially those rich in cyclohexane derivatives, and of the C_5 , C_6 , and C_7 hydrocarbons results in a gas stream containing a high percentage of butadiene in the four-carbon fraction. The over-all yield is such as to make deliberate synthesis by this means uneconomic, although in wartime a small amount was made this way as a quick stopgap during dehydrogenation plant construction.

Butadiene is manufactured from ethanol, by dehydrogenation to acetaldehyde and further reaction of more ethanol with the acetaldehyde, in a second step catalyzed by silica-tantalum, silica-zirconium and similar catalysts:

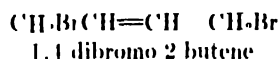


The reaction may also be accomplished in a single step. Crotonaldehyde is an intermediate. About 215,000 tons of annual capacity was installed in the U. S. wartime program, but due to the cost of the alcohol feed stock, was generally uneconomic to operate in comparison with the petroleum-based processes.

Butadiene may also be produced from acetylene, by hydration to acetaldehyde, which then goes through the intermediates aldol and 1,3 butylene glycol in order, or by condensation with formaldehyde to butyne-2-diol-1,4($\text{C}_4\text{H}_6\text{O}_2$) which is then reduced and dehydrated. Butadiene production in Germany is founded on this reaction.

Isolation and purification of butadiene from the dilute mixtures in which it is produced in cracking and dehydrogenation processes is difficult because of the close boiling points of the four carbon hydrocarbons, and azeotrope formation. Extractive distillation and solvent extraction are extensively used. Furfural is extensively used as the solvent in commercial plants. Water and dimethyl formamide are also very selective. Much of the commercial production employs the reaction of butadiene with cuprous ammonium acetate solution, in which a solid addition complex is found. Butadiene is regenerated by decomposing the complex by gentle heating. Butadiene may also be separated by formation of a crystalline sulfone with sulfur dioxide. The butadiene produced in the United States is 98.0% or better purity. Acetylene and heavier hydrocarbon contents are both kept below 0.1% and only a few parts per million of peroxides and carbonyl compounds are present.

The importance of butadiene is due to its great reactivity as a conjugated diene. The unsaturated linkages add halogens, water, hydrogen, ozone, etc., may be oxidized to glycols, acids, etc., in normal manner with either one or both of the double bonds reacting. Aromatics may be alkylated, as in the production of butenyl benzene from benzene. Butadiene undergoes the typical 1,4 addition reactions of conjugated dienes, in which the remaining double bond shifts to the central position:



It also undergoes the diene condensation, or Diels-Alder reaction, in which 1,4-addition takes place on an activated double bond. The double bond in maleic anhydride is activated by the two adjacent carbonyl groups. Condensation with a wide variety of unsaturated aldehydes, nitriles, etc., occurs. A similar condensation with another molecule of butadiene produces the dimer 4 vinyl-1 cyclohexene.

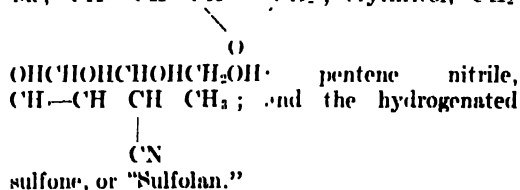
Along with isomeric dimers it forms in butadiene in storage, quite rapidly above 40°C. Butadiene owes its greatest importance to its ability to polymerize readily under the influence of various catalytic systems and to copolymerize with a wide variety of compounds containing a vinyl group. Bulk or mass polymerizations are carried out with sodium, sodium alkyl-sodium alkoxide combinations (Alfin catalysts) and ionic materials such

as boron trifluoride, hydrogen fluoride, aluminum chloride, etc. Free radical generating systems, such as peroxides, persulfates, and "redox" catalysts generally are employed with the butadiene emulsified. A wide variety of polymers may be produced varying from short linear chains to highly branched, cross linked and cyclized materials. Low molecular weight polymers are viscous liquids; rubbery, soluble solid polymers are most commonly made; highly cross linked types are resinous, insoluble, and are often of the self-propagating or "popcorn" type.

The principal uses of butadiene are in polymers. Substantially all the government production has been used to make GR-S synthetic rubber, a 75/25 copolymer with styrene produced in an aqueous emulsion at either 122 or 41 F ("Cold Rubber"). A soap is used as the emulsifying agent and potassium persulfate as the initiating agent. Most of the polymer is coagulated to a crumb by addition of salt and acid, but some is used in the form of latex, foam rubber, elastic-coated thread, etc. Oil resistant copolymers are made with acrylonitrile, and other special copolymers tailor-made for definite uses are produced in small amounts. Butadiene-styrene copolymers of high styrene content are produced privately for use in rubber base emulsion or "latex" paints and for shoe sole compositions. Liquid butadiene polymers are finding increasing use as drying oils, in baked metal enamels and upgrading of vegetable drying oils.

Butadiene is used as the basis for one process for nylon manufacture. It is chlorinated to the 1,4 dichlorobutene, reacted catalytically with hydrogen cyanide and hydrogenated to adiponitrile. By further hydrogenation hexamethylene diamine, one of the components of the polyamide fiber is produced; an adipic acid, the other component may also be produced by hydrolysis if desired.

Certain diene condensates are finding specialty uses. Tetrahydrobenzaldehyde is produced when acrolein is used and finds use as an anti enzyme in toothpaste. A bimolecular condensate with furfural is used as an insect repellent. Other products available from butadiene include the monoxide, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$; erythritol, CH_2-



In 1953, butadiene produced for government account, primarily for GR-S, was 1,051,468,000 pounds. Production for private account was 100,729,000 pounds additional.

J. C. HILLYER

Cross-references: *Dienes, Diels-Alder Reaction, Polymerization*

CADMIUM AND COMPOUNDS

The element cadmium was first discovered by Strohmeyer in 1817. It is a relatively rare element; its abundance in the lithosphere is estimated in the order of 0.5 gram per ton of the earth's crust. Cadmium minerals are rarely found alone; they are usually associated with zinc minerals.

Cadmium is in Group II, Period V of the Periodic Table. It has eight isotopes ranging from 106 to 116 in mass. Other physical constants are presented below:

Atomic number	48
Atomic weight	112.41
Color	Silver-white
Crystal structure	Hexagonal pyramids
Hardness (Mohs)	2.0
Ductility	Considerable
Density (g/cc)	
20°C (68°F) (s)	8.65
330°C (626°F) (l)	8.01
Melting point	321°C (609.8°F)
Boiling point	767°C (1412.6°F)
Specific heat (g-cal/g)	
25°C (77°F) (s)	0.055
Electrochemical equivalent	0.582
Cd ⁺⁺ (mg/coulomb)	
Electrode potential Cd ⁺⁺	-0.40 volt
(H ₂ = 0.0 volt)*	

* National Bureau of Standards nomenclature.

The major sources of cadmium are from zinc ores in various parts of the globe. The more important deposits are in Australia, Tasmania, Belgian Congo, Canada, Mexico, Peru, Southwest Africa, Western United States, and the Tri-State District (Missouri-Oklahoma-Kansas).

Mexico is probably the largest primary source of cadmium-bearing ores on the basis of quantities mined. It should be emphasized that practically all the cadmium obtained is as a by-product of zinc recovery and the supply of cadmium is dependent on the amount of zinc which is extracted; however, not all zinc ores contain cadmium.

The present world production of cadmium is in the order of 15 million pounds, of which a large proportion is recovered in the United States. At the present time, cadmium is quoted at \$1.70 per pound. Most cadmium is recovered from primary sources. Only small amounts are recovered from secondary metals.

A large proportion of the cadmium is recovered from zinc sulfide ores. These ores are roasted to crude oxide, mixed with coal or coke and sodium or zinc chloride and passed over a sintering machine. Combustion of the coal provides the necessary temperature in the sintering bed to allow

reaction of the chlorides with cadmium, lead, and some other impurities; these impurities are volatilized and collected, usually in an electrostatic precipitator. These chlorides are then reacted with sulfuric acid, solubilizing the cadmium. The cadmium is then removed from solution by careful selective precipitation with zinc dust; the cadmium sponge from this operation is then compressed (to prevent excessive oxidation) and distilled. This crude cadmium is then redistilled and sometimes chemically purified. It is then cast into slabs or special shapes.

Complex ores containing cadmium (almost invariably associated with zinc) require special treatment but use the same general principles. Another source of cadmium is in the purification of zinc sulfate liquor for electrolytic recovery of zinc. Prior to the electrolysis of the zinc sulfate solution, cadmium is removed by selective precipitation with zinc dust and the cadmium is then purified as previously described. In some cases the final step in recovering cadmium is effected by electrolysis of a cadmium sulfate solution.

Cadmium is almost always divalent. It slowly oxidizes in moist air at room temperature. At higher temperatures, the oxidation is more rapid. Cadmium reacts with the halogens to form the corresponding halides, chlorine being the most reactive. Cadmium is soluble in most acids but, unlike zinc, is not soluble in alkalis. It has good corrosion resistance except in acid environment. It is this resistance which makes cadmium coatings so effective in retarding corrosion.

The fumes of cadmium and its compounds, as well as solutions of its compounds, are poisonous. The toxicity of cadmium has not been fully appreciated and unwitting exposure to cadmium fumes is probably responsible for many cases of poisoning. Adequate precautions, such as the use of good respirators in the presence of cadmium fumes, will prevent the vast majority of poisonings. It can not be too strongly emphasized that cadmium has highly lethal potentialities.

The major use of cadmium is for plating articles to give a protective coating (mainly for iron and steel); most of this coating is done by electrodeposition. Practically all commercial plating is done from cyanide baths which are essentially a solution of cadmium oxide and sodium cyanide in water. Cadmium coatings have good resistance to atmospheric and galvanic corrosion and to alkalis, but their resistance to acid attack is poor.

A wide variety of both small and large parts for many uses are cadmium plated for such protection. However, cadmium is almost never used in equipment or in containers for food or drinks, in view of its toxicity.

Cadmium alloys with a large number of other metals. This property is responsible for another use of cadmium although smaller quantities are used than for electroplating. Cadmium alloys are used for high temperature, high-speed bearing metals. Other alloys are used for high-temperature solders, and still another series of alloys is used for low temperature applications.

Cadmium is one of the more efficient absorbers or capturers of neutrons and, as such, finds utility in atomic work. It is used in the control of nuclear reactions and can also be used as a shield to prevent escape of the neutrons. The isotope Cd^{113} is especially effective for such purposes.

A small but important scientific use of cadmium is in the Weston standard cell, which is the working standard for the United States in maintaining the value of the volt. Another electrolytic couple is the nickel-cadmium storage battery in which the negative is cadmium and the positive is nickel oxide, the electrolyte being an aqueous solution of potassium and lithium hydroxides.

The most important cadmium compound is cadmium sulfide, usually prepared by precipitation of cadmium in solution with the sulfide radical. Cadmium sulfide is a brilliant yellow and is used as a pigment. Colors varying from yellow to a brilliant red can be secured by replacing an increasing proportion of the sulfide radical by selenium. Still another cadmium pigment is cadmium lithopone, prepared by co precipitation of barium sulfide and cadmium sulfate; proper proportions of these two materials give pigments from light yellow to deep red. The cadmium pigments range in price from about 50 cents to \$1.50 per pound.

Cadmium sulfate and its hydrates are made by reaction of the metal or oxide with sulfuric acid. It is used in medicine, for fluorescent screens, and as an electrolyte in the Weston standard cell.

Cadmium oxide is commercially prepared by oxidizing cadmium vapor with air. Its major use is as an ingredient of electroplating baths and in the manufacture of pigments.

JOHN R. MURGRAVE

CALCINATION

The process of calcination, in its broadest usage, is the heat treatment of a solid material to bring upon a stage of thermal decomposition or phase transition other than melting. In its original connotation the term implied a thermal dissociation process involving the separation of volatile from nonvolatile components, the term being derived from the alchemist method by which lime (calx) was obtained from limestone by ignition. In modern industrial usage calcination processes have subsequently come to include the following types of reactions:

(1) Thermal dissociation reactions such as the decomposition of oxy-salts and hydrates; pyrolysis and destructive distillation of organic compounds. Examples: the concentration of alumina by ignition of bauxite (aluminum hydroxides) ores to ca. 1100°C ; the decomposition of the carbonate

or hydroxide of calcium to yield lime, carbon dioxide, and water on heating above 545°C and 890°C , respectively; coking and coal gas recovery from bituminous coals heated over the range 500 to 1200°C .

(2) Thermal polymorphic phase transitions. Examples: the conversion of pigment grade anatase to the rutile form of titanium dioxide above ca. 700°C ; the alpha-beta quartz transition at 573°C , the consequent volume changes aiding in the process of disintegrating sandstone and quartzite type rocks.

(3) Thermal recrystallization. Examples: the crystallization of mullite for refractory use from coprecipitated alumina-silica gels heated to above 1100°C ; the conversion of activated (amorphous) magnesia to periclase above 1650°C ; devitrification of glass.

Calcination is often the initial beneficiation treatment in the processing of many metallic and nonmetallic ores. The treatment will frequently serve for both a preliminary chemical concentration through loss of volatiles and, as a result of accompanying volume changes, for producing a friable physical structure. The calcination reaction is also frequently used to activate a material for a simultaneous reaction with admixed solids as in the manufacture of portland cement and calcium carbide. The attainment of a highly reactive material in controlled calcination is the basis of numerous solid state syntheses of high melting point ceramic-type materials from oxy-salt starting materials and the oxides silica, alumina, and titania, among others of commercial interest. A preliminary calcination is often used in the ceramic and allied industries to reduce excessive firing shrinkage and resultant warpage and breakage of ware. In numerous metallurgical applications, heterogeneous phase reactions involving interaction with the furnace atmosphere are carried out simultaneously with the calcination of the ore. Processes resulting in oxidation are known as roasting. Reduction reactions resulting in the separation of a metal phase are classified as smelting.

For the most part the temperatures employed and the degree of calcination of commercial materials are dependent upon the type of product desired as well as upon the nature of the raw material. Caustic magnesite for use as a rubber accelerator is the product of calcination of the carbonate between 700 and 1000°C . The product contains from 2 to 5% residual carbon dioxide. Dead-burned magnesite for use as a basic refractory is a sintered, inert product obtained by small additions of iron oxide to the crude carbonate heat treated over the range 1450 to 1700°C . The product contains less than 0.5% residual CO_2 .

The industrial technology of modern lime and magnesia calcination processing is impressive. The size of the most commonly used rotary type kilns have reached up to 12 feet in diameter and up to 500 feet in length. Production rates in the lime industry have attained in excess of 250 tons of lime per day operating at temperatures from 1100 to 1350°C . The kilns are usually oil- or gas-fired, increased thermal efficiencies being obtained

by passing the exhaust gases over the feed intake bed. Calcination rates and type of product are closely controlled by selection of raw materials, adjustments in temperature, air draft, load, rate of rotation and the inclination of the kiln.

S. S. FLASCHEN

Cross-references: Calcium

CALCIUM AND COMPOUNDS

Calcium is a white, silvery alkaline-earth metal, in Group II of Periodic Table, with atomic number 20 and atomic weight 40. It tarnishes in air with the formation of thin bluish gray films of oxide. These films are tight, adherent and protective. Commercial electrolytic calcium in the form of a slab 2 in. thick, exposed to the atmosphere under average conditions, corroded to a depth of $\frac{1}{4}$ in. in six months' time. Calcium may come into contact with the skin without danger, and can be machined, cut, extruded or drawn. It is commercially available as the direct product from the electric furnace, as a remelted material, or as a sublimed material.

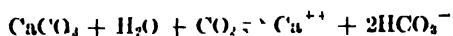
Calcium is made by the electrolysis of fused calcium chloride, or by thermal processes under high vacuum from lime reduced with aluminum. The Downs cell for the electrolysis of fused salt produces a sodium metal containing calcium. The calcium crystallizes out of solution and is filtered from the liquid sodium. This is a third commercial source of calcium metal and calcium-sodium material.

Calcium metal is employed as an alloying agent for aluminum, bearing metals of the lead-calcium or lead-barium-calcium type; as a reducing agent for beryllium; as an alloying agent and a deoxidizer for copper; an alloying agent for the production of the age hardening lead alloys for cable sheaths, battery plates, and related uses; a modifying agent for magnesium and aluminum; a debismuthizer for lead; a controller for graphitic carbon in cast iron; a carburizer and desulfurizer, as well as a deoxidizer for numerous alloys such as chromium-nickel, copper, iron, iron nickel, nickel, nickel-cobalt, nickel-chromium iron, nickel bronzes, steel and tin bronzes; an evacuating agent; a reducing agent in the preparation of chromium metal powder, thorium, uranium, and zirconium; and a separator for argon from nitrogen. Typical of these applications is the addition of 0.25% calcium to magnesium alloys to refine the grain structure, reduce the tendency to take fire, and to modify the strengthening heat treatments.

Calcium oxide is commonly prepared by burning the carbonate in large vertical shaft kilns at temperatures below 1200°C. It is a white solid, often called quicklime. It slakes or reacts with water to form the hydroxide $[\text{Ca}(\text{OH})_2]$, a common constituent of mortars and plasters, and an industrial alkali and neutralizer for acids.

Limestone is calcium carbonate in an indistinctly crystalline and massive form. It is found through-

out the United States, but extensive deposits exist in Indiana. All varieties of calcium carbonate are almost insoluble in pure water but dissolve appreciably in the presence of carbon dioxide because of the formation of calcium hydrogen carbonate (bicarbonate):



It is by this reaction that limestone is dissolved, often resulting in the formation of caves. Natural waters containing CaCO_3 are called hard waters or limestone waters. The action is reversible; and in many regions the underground waters, carrying large quantities of the carbonate, lose carbon dioxide on exposure in caves and deposit limestone. Travertine, used as a building stone, is a white concretionary calcium carbonate deposited by some springs when the pressure on the water is suddenly released, permitting the rapid escape of carbon dioxide.

Calcium fluoride, as the mineral fluorite or fluorspar, is the commercial raw material for hydrofluoric acid and fluorinated organic compounds such as the "Freons."

Calcium chloride occurs in nature as tachhydrite $[\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}]$, and in some other minerals and also to the extent of about 0.15% in sea water. A considerable amount is removed from salt brines. It is a byproduct of the Solvay soda and other industrial processes. Upon evaporation of its aqueous solution the hexahydrate $[\text{CaCl}_2 \cdot 6\text{H}_2\text{O}]$ is obtained, and by partial dehydration it is converted into a porous mass which is used for drying gases and liquids. Calcium chloride is very soluble in water; for this reason it gives with ice an excellent freezing mixture. With the hexahydrate and crushed ice a temperature as low as -50°C can be reached. A solution of the salt is used as a refrigerating brine in cold storage plants and in the manufacture of ice. Because of its deliquescent property it is sprinkled on roads to lay the dust and (in solution) in mines to decrease the danger of explosion from dust.

Anhydrous calcium sulfate occurs in nature as the mineral anhydrite, crystallized in rhombic prisms. The dihydrate, or gypsum $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$ is, however, more common and plentiful. Three general groups of gypsum products—uncalcined, calcined building, and calcined industrial—are sold. Uncalcined gypsum is used as a portland cement retarder to prevent too rapid hardening, and as a soil corrector in agriculture. Calcined gypsum is employed in making tile, wallboard, lath, and various kinds of plasters. When gypsum is heated to about 125°C it loses three fourths of its water of hydration and forms the hemihydrate $(2\text{CaSO}_4 \cdot \text{H}_2\text{O})$ or plaster of Paris. The resulting product is ground to a fine white powder. When this is mixed with water it forms a plastic mass which quickly sets to a coherent white solid consisting of small tangled crystals of more highly hydrated calcium sulfate.

Calcium metaphosphate is widely used as a mild abrasive and neutralizer in tooth pastes.

CHARLES L. MANTELL

CALORIMETRY

Calorimetry is the science of measuring the quantity of heat absorbed or evolved by matter when it undergoes a change in its chemical or physical state. The apparatus in which the measurement is performed is a calorimeter, and the experimenter is frequently referred to as a calorimetrist.

When matter is involved in a chemical or physical process, its total energy content is usually altered. The difference in energy between its initial and final states, ΔE , must be transferred to, or from, the environment of the system. This energy exchange between the system and its environment is in the form of heat or work or both. In calorimetry, the energy exchanged as heat is quantitatively evaluated. The heat absorbed by the system, q , is related to the work done by the system on its environment, w , and the increase in internal (total) energy of the system, ΔE , by the thermodynamic relationship

$$q = \Delta E + w \quad \text{Eq. (1)}$$

When calorimetric measurements are performed at constant pressure and only pressure-volume work is involved, q is equal to the increase in heat content or enthalpy, ΔH . Most calorimetric measurements are performed under these conditions, but when other conditions are imposed, appropriate consideration must be made in the thermodynamic treatment of the data.

The process selected for calorimetric study may be a simple change in the physical state of matter, such as a change in temperature of the material, or it may consist of a series of complex chemical reactions such as are encountered in the combustion of many fuels. In fact, nearly any process involving a chemical or physical change in matter might well become a necessary subject for calorimetric investigation.

Calorimetric determinations of energy changes are essential in many theoretical and practical problems. Heat capacity or specific heat data are vital to the design of heat exchange equipment. The thermal properties of steam and certain metals are a major consideration in the design of modern boilers and turbines. The heats of combustion of fuels are essential in rocket, engine and gas turbine design. The heat liberated by chemical reactions must be considered in the development of chemical process equipment. Often the required equilibrium constant of a process is most conveniently obtained by a simple calculation from the free energy change, ΔF . For a great many processes, numerical values of ΔF can be obtained from the change in heat content, ΔH , and the entropies of the participating substances, S , using the thermodynamic relationship

$$\Delta F = \Delta H - T\Delta S \quad \text{Eq. (2)}$$

where T is the absolute temperature. The entropies of the individual substances can generally be evaluated from heat capacity measurements that extend to very low temperatures.

The design and constructional details of calo-

rimeters vary widely because of the diversified nature of the processes suitable for calorimetric study. However, the basic principles are general and their consideration constitutes a common requirement in practically all designs. Suitable devices and procedures for three essential measurements are usually required, but one or two can sometimes be omitted by operating under certain restrictions. The measurements are: (1) the temperature of the calorimeter and its contents, (2) the quantity of energy that is added to the calorimeter from an external source, and (3) the quantity of heat that is exchanged between the calorimeter and its environment.

Most calorimetric operations involve a temperature change, since the heat liberated (or absorbed) during the process is stored in the calorimeter and its contents by virtue of their combined heat capacity. Thermocouples, thermopiles and resistance thermometers are commonly used for temperature measurements. The quantity of energy liberated or absorbed in a calorimetric process is evaluated in terms of electrical energy. This is done by three similar methods. (1) In an exothermic process where heat is liberated, the calorimeter is cooled to the original temperature; the temperature rise is then duplicated using an electrical resistance heater. (2) The heat absorbed in an endothermic process is supplied by an electrical heater at such a rate as to keep the temperature constant. (3) In heat capacity measurements, the electrical energy is supplied directly by a heater. Electrical energy and temperature can be measured very accurately by modern methods, but the problem of heat transfer between the calorimeter and its environment is more difficult. The minimization of, and accurate correction for, heat exchange is the major problem to be reckoned with in modern calorimetry.

When two adjacent bodies (such as a calorimeter and its environment) are not at exactly the same temperature, heat is transferred from the warmer to the cooler body. In calorimetry the transfer is made by three major processes: (1) gaseous convection, (2) conduction, and (3) radiation. Gaseous convection can be completely avoided by evacuating the space between the calorimeter vessel and its environment. When evacuation is impractical, convection can be minimized by suitable geometrical considerations in the design of the calorimeter. It is very important to avoid or at least minimize convection, since the heat transported is a complex function of the temperature difference and an accurate evaluation is impossible. Conduction by air or other gases is also usually minimized by evacuating as much as possible of the space between the calorimeter proper and its environment. Conduction in solid materials, used for supporting the calorimeter and for electrical leads, is minimized by proper choice of materials and geometrical design. For small temperature differences, radiation is usually not a serious problem at low temperatures but is a major contributor to heat exchange at elevated temperatures. Heat exchange by radiation can be limited to a few per cent of the blackbody (maxi-

mum) values by the use of suitable reflecting surfaces on the outside of the calorimeter and on the adjacent environment. In the absence of convection and for small temperature differences, the heat transferred, Q , is essentially proportional to the temperature difference, ΔT , and time, t , in accordance with Newton's law of cooling.

$$Q = k\Delta Tt \quad \text{Eq. (3)}$$

It is apparent that anything that can be done in calorimeter design and operation to minimize the terms on the right hand side of Equation 3 will aid in decreasing the quantity of heat exchanged. Adiabatic calorimeters are operated on the principle that there is no heat exchange, and thus no correction to evaluate, if the calorimeter and its environment are maintained at the same temperature.

In calorimeters containing liquids there is a possibility of a fourth mechanism for transporting heat. This method involves the transport of matter from the calorimeter and its subsequent condensation on the surrounding surfaces. The effect can be avoided by keeping the environment warmer than the liquid or by completely enclosing the liquid. However, even in a completely enclosed system the possibility of vaporization into the space above the liquid with increasing temperature must be considered for volatile liquids.

There are many different varieties of calorimeters, each being particularly suited for a specific type of measurement. Some general features of several representative types are discussed below.

Low-temperature calorimetry has become an important source of heat-capacity data for the evaluation of entropies of substances from measurements extending from near the absolute zero to room temperature or slightly above. The calorimetric vessel consists of a vacuum-tight metal container in good thermal contact with an electrical resistance heater and a thermocouple or resistance thermometer. The sample under study is sealed in the container along with a small amount of gaseous helium. The helium aids in attaining thermal equilibrium at low temperatures because of its high thermal conductivity. The calorimetric vessel is suspended in an evacuated chamber by some material, such as strong thread, having low thermal conductivity. This chamber is often within a massive copper block which provides a uniform and stable thermal environment. The temperature of the protective block is kept at a temperature near that of the calorimetric vessel. The heat exchanged is evaluated by observing the temperature difference, ΔT , as a function of time and applying Equation 3 in an integrated form. The constant, k , is evaluated by observing the change in temperature of the calorimeter vessel and its contents under equilibrium conditions. During this rating period the temperature change is due entirely to heat exchanged with the environment. Some calorimetrists use the adiabatic principle and maintain the temperature of a protective shield as near as possible to that of the calorimeter. This procedure results in the elimination of heat exchange corrections but is not en-

tirely free from objections. Although low temperature calorimeters are used chiefly for heat capacity determinations, heats of transition, heats of fusion, and heats of vaporization are also measured.

The dropping method is the most common of the accurate high temperature procedures for measuring heat contents. This apparatus consists of a carefully regulated furnace and a suitable calorimeter, such as a Bunsen ice calorimeter, operating near room temperature. The sample under investigation is sealed inside of a container that will not undergo chemical reaction at the highest temperature of the measurements. The sample and container are thermally equilibrated with the furnace and then dropped into the calorimeter. The empty container is studied in an identical manner and the difference in the two measurements gives the heat content of the sample relative to the room temperature reference. Heat capacities are derived from a series of such measurements as a function of temperature and the thermodynamic relationship:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = \left[\frac{\partial (H - H_0)}{\partial T} \right]_p \quad \text{Eq. (4)}$$

where C_p is the heat capacity at constant pressure, H the heat content, H_0 the heat content at the reference temperature, and T the absolute temperature.

The Bunsen ice calorimeter is an example of an isothermal calorimeter that is operated at a fixed temperature. The calorimeter is usually surrounded by ice, making it also adiabatic and thus free from heat exchange. Bunsen's design makes use of the very large difference between the specific volume of ice and water. The calorimeter contains a closed chamber which is full of ice and water. A pool of mercury is maintained in the bottom of the chamber and as the ice melts, additional mercury enters and keeps the chamber full. The calorimeter has a universal calibration in the form of energy per unit mass of mercury. In early versions, the quantity of ice melted was used as a measure of the heat liberated in the calorimeter. By replacing the ice with other suitable substances the restriction of operating at one fixed temperature can be removed.

Quantitative measurements of the heat liberated (or absorbed) during the solution of a solid or of another liquid by a solvent are performed in solution calorimeters. Heats of solution, dilution and mixing are common determinations of this type. In addition to participating in the process under investigation, the solvent is used as a means of attaining uniform temperature and composition throughout the calorimeter. This feature necessitates stirring, which is usually accomplished with mechanically or magnetically driven stirrers. Sometimes, however, the calorimeter itself is rotated. Regardless of the method used, the quantity of heat introduced by the stirring must be determined either directly or indirectly and a suitable correction must be applied. Another feature characteristic of solution calorimeters is the method of adding the sample. It must

either be equilibrated with the solvent in the calorimeter or its heat content relative to the calorimeter temperature must be determined. A common method for solids is immersing a capsule containing the sample in the solvent and breaking it at the desired time.

The heat of combustion of fuels and similar materials is usually measured by bomb calorimetry. The solid or liquid sample is contained in a bomb (pressure vessel) containing excess oxygen, or other suitable gas under pressure. The bomb is immersed in a calorimeter containing a liquid, usually water. The reaction is initiated by igniting the sample with a measured amount of electrical energy, and the heat evolved is measured in terms of the temperature rise of the calorimeter. Electrical energy is usually used to duplicate the temperature rise and thus evaluate the heat liberated. However, sometimes a standard sample of a substance having a known heat of combustion, such as benzoic acid, is used to calibrate the apparatus. In bomb calorimetry corrections to standard conditions must be applied (Washburn corrections) since the system is under pressure and because solutions are usually formed.

There are many other important types of calorimeters, such as flow calorimeters, microcalorimeters, flame calorimeters, etc. Nearly any process can be studied by the investigator who is ingenious enough to devise the appropriate apparatus and who has the resources and patience to undertake an extensive project. Although calorimetric measurements are in general time-consuming and tedious, they are essential for a fundamental and practical understanding of many important chemical and physical processes.

J. E. KUNZLER

Cross-references: *Thermodynamics*

CANNIZZARO (1826-1910)

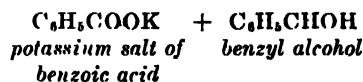
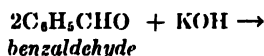
Cannizzaro based his principles on Avogadro's law—that under the same conditions the number of molecules is proportional to the volumes of gases, that is, equal volumes of gases contain the same number of molecules, assuming like conditions of measurement. As a consequence, the densities of gases are proportional to their molecular weights. For example, nitrogen gas weighs 1.25 g/liter at STP and hydrogen 0.09 g/liter. $1.25/0.09 = 14/1$. Nitrogen molecules are 14 times as heavy as hydrogen molecules.

Cannizzaro pointed out the distinction between atoms and molecules. He showed that the principle of Dulong and Petit (atomic weight \times specific heat = 6.4) is a useful method of finding atomic weights. He also understood that if several compounds of two elements contain a fixed amount of one element, then the smallest proportional weight of the other element is its atomic weight. In other words, if several compounds contain two elements, and the atomic weight of one of them is known and taken as a reference quantity, then the smallest combining weight of the other element is its atomic weight.

The work of Cannizzaro in clarifying atomic

weights led directly to the classification of the elements by Mendeleeff (1834-1907) and the discovery of the periodic law.

Cannizzaro was also an organic chemist of considerable reputation. He published over eighty papers, and 56 of them are in the field of organic chemistry. Probably his most notable discovery is that of the reaction that bears his name—the simultaneous self-oxidation-reduction of an aldehyde in the presence of concentrated alkali. Cannizzaro's reaction is well known for benzaldehyde and other aldehydes that have no hydrogen on the alpha carbon atom (the carbon atom next to the aldehyde group). For example:



Cannizzaro was elected to the Royal Society (London) in 1862 at age 36, and was awarded the Copley medal by that body in 1891. His seventieth birthday was celebrated appropriately, including a letter from the American Chemical Society.

ELBERT C. WEAVER

Cross-references: *Avogadro, Mendeleeff*

CARBIDES

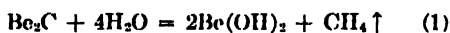
General Binary Compounds of Carbon

The term "carbide" has a content of popular meaning which does not correspond to any natural classification. For the purpose of this article the term "carbide" is defined as a binary compound of carbon and any other element. The elements of the major portion of the Periodic Table form carbides according to this definition. Broad as this definition is, it is probably too confining in certain instances. Thus the compound cohenite $(\text{Fe}, \text{Ni})_3\text{C}$ is isomorphous and closely related to cementite (Fe, C) but definitely is not included in the above definition. In other cases the definition may seem too broad, as it regards carbon tetrachloride (CCl_4) or carbon monoxide as carbides.

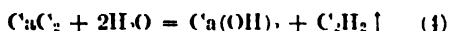
Two general factors have central importance for the determination of the chemical and physical properties of the carbides. The first is the electronegativity difference between carbon and the element in question, as defined by Pauling. The second factor is the presence or absence of an uncompleted electronic "d" or "f" shell; i.e., whether the element in question belongs to one of the transition series. These two factors form the main basis for the method of classification here employed. It emphasizes the basic characteristic differences among the carbides and groups together those carbides with common properties.

Salt-like carbides. These carbides are characterized by a large electronegativity difference between carbon and the element involved, ranging between +1.8 to +1.0. They react with water to form the hydrocarbon corresponding to the chain length and to the valence of the carbon assembly

within the crystal. Thus we have the methanides Be_2C and Al_4C_3 , which react to form pure methane according to the reactions:



The acetylides are widely represented in the Periodic Table among the alkali metals and alkaline-earth metals. They have the formulas M_2C_2 and MC_2 . The reactions of sodium carbide and calcium carbide with water occurs violently.



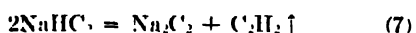
Finally there is the very remarkable compound *magnesium carbide* which on hydrolysis yields methyl acetylene according to the reaction:



When acetylene is passed through a solution of sodium in liquid ammonia a sodium acetylide is formed according to the reaction:



Similar reactions occur for the liquid ammonia solutions of potassium and lithium. On heating the sodium acid acetylide to 180°C , sodium acetylide is formed:



The action of the electric arc on lithium carbonate yields lithium acetylide. With the possible exception of sodium, the other alkali metals do not form acetylides by the direct reaction with carbon even at high temperatures.

The acetylides of the alkaline earth metals are in general prepared by the direct action of the element on one of its compounds on carbon at high temperatures in an electric arc or blast furnace. Specifically carbon and calcium oxide form calcium carbide at 1800°C . Calcium acid acetylide like the corresponding sodium acid acetylide can be formed by the action of acetylene on the solution of calcium in liquid ammonia. It too will decompose into the dibasic acetylide by heating. Magnesium carbide (MgC_2) is obtained as the product of the reaction between magnesium and ethane at $450-500^\circ\text{C}$, but the carbide of the formula Mg_2C_3 is best obtained as the product of the reaction between magnesium and pentane at 650°C .

The *unstable salt like carbides* are represented by the three compounds Cu_2C , Ag_2C_2 , and Hg_2C_2 . They too can be regarded as salts of acetylene. They are synthesized by the reaction of acetylene with aqueous solutions of cuprous, argentous, and mercurous salts. By hydrolysis the acetylene can be again regenerated. These carbides differ from the other salt-like carbides in that they are explosive. For this reason they cannot be prepared by the direct action of carbon on the metal. The differences may be ascribed to the low electronegativity difference between carbon and copper, silver and mercury which is of the order of 0.8. The bonds thus have very little ionic character. Silver acetylide and cuprous acetylide are used commercially as detonators.

Cross-linked covalent carbides. Carbides falling within this category have electronegativity differences of 0.7 to 0.0. They are represented by boron carbide B_4C , silicon carbide (SiC), diamond, and possibly the carbides of arsenic and phosphorus PC_3 and AsC_3 . The first three at least are composed of crystals which are uniformly covalently linked together so that every crystal represents a single giant molecule in the same sense that the word molecule is used in organic chemistry. This fact accounts for the tremendous hardness of these compounds. Thus B_4C has a hardness of 9.5 on the Mohs scale of hardness, and SiC , 9.0. On the same scale sapphire or corundum has a hardness of only 9.0.

Boron carbide reacts rather readily at $900-1000^\circ\text{C}$ with chlorine gas to form boron trichloride. This has made it useful in the past as the starting point of total syntheses of boron compounds. Recently elemental boron has become commercially available for this purpose. This property of unusual hardness makes these compounds very important commercially as cutting, wear resistant, and abrasive materials. Boron carbide can be synthesized by the interaction of boron oxide, (B_2O_3) and carbon at $2500-2600^\circ\text{C}$. *Silicon carbide* is made commercially from silica and carbon at temperatures of 2200 to as high as 3000°C . Until recently diamonds were obtained only as a natural mineral. Very recently very small diamonds have been produced synthetically under controlled and reproducible conditions at pressures of 800,000 psi and advanced temperatures.

Volatile covalent carbides. The volatile covalent carbides are closely related to the cross linked covalent carbides.

Cyanogen (C_2N_2), is a colorless poisonous gas. The chemistry is very similar to that of the halogens. At 400°C it polymerizes to form a solid paracyanogen (CN). This tendency to polymerization shows the relation of cyanogen to the cross linked covalently bound carbides.

Carbon monoxide (see **Carbon Monoxide** article).

Carbon dioxide (see **Carbon Dioxide** article).

Carbon disulfide is a heavy, colorless, flammable, poisonous liquid. It reacts with chlorine to form carbon tetrachloride in commercial quantities. It is formed by the direct union of carbon and sulfur in the electric furnace.

Carbon diselenide has been prepared by the action of hydrogen selenide on carbon tetrachloride, forming carbon diselenide and hydrochloric acid.

The evidence for carbon ditelluride is somewhat unsatisfactory. The compound is thought to be formed when an arc is formed between tellurium and graphite electrodes under carbon disulfide.

The carbon tetrahalides are characterized by chemical inertness which can be related to their approximation of the electronic configuration of the rare gases. The stability of these halides decreases as one passes from CF_4 to CI_4 in the Periodic Table. *Carbon tetrafluoride* is a colorless inert gas. Commercially it is formed in the preparation of aluminum during the electrolysis of cryolite. *Carbon tetrachloride* is a colorless, heavy, inert

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Fig. 1. Classes of the carbides, characteristic formulas, and the Pauling electronegativity difference of the carbon-element bond and their relation to the Periodic Table (Courtesy of Bureau of Mines, U. S. Department of Interior)

liquid widely used as a solvent and as a fire extinguisher. *Carbon tetrabromide* and *carbon tetrachloride* are heavy inert liquids often used as standards for the refractive index measurement of high refractive index materials.

Stable carbides of the transition elements. These carbides possess metal atom arrangements of either the face-centered cubic or hexagonal close-packed type. The carbides of the formula MC' generally possess the former structure and those with the formula M_2C' the latter. In addition to these, there are carbides of the formula MC'_2 which seem to form only with elements of either

the lanthanide series (rare earths) or actinide series of elements. The MC'_2 carbides have crystal structures closely related to that of calcium carbide in that each occupied interstice contains two carbon atoms.

The stable carbides are characterized by exceedingly high melting points, unusual tensile strength and hardness, and considerable inertness to acids. The type of bonding responsible for these properties has been the subject of considerable speculation.

The actinide and lanthanide carbides UC'_2 , ThC'_2 , LaC'_2 , NdC'_2 , and probably others upon

treatment with water or acids produce some acetylene but mainly hydrogen and more saturated hydrocarbons. The C_2 group in these compounds cannot therefore be regarded as a true acetylide ion, or alternately the hydrogenation power of the rest of the compound must be such that acetylene cannot be liberated as such. The fact that divalent ions of the rare earth elements are not ordinarily produced in aqueous solutions may also be involved.

The uranium carbides UC and UC_2 can be synthesized by the action of carbon on uranium metal at 2100 and 2400°C respectively. UC can also be formed by the action of methane on very finely divided uranium (prepared by the decomposition of uranium hydride) at 450°C. Most of the other refractory carbides can be formed by the direct combination of the metal and carbon at about 2200°C.

Commercially the hardness of some of these compounds is employed in carbide cutting tools where they are generally used in a matrix of cobalt metal. These compounds are also formed in tool steels where their presence insures the hardness and the hot work characteristics of these steels.

Unstable carbides of the transition elements. Most of these carbides have unusual and complex structures, although a few have the same structures as the stable carbides. Examples of the latter are the hexagonal close-packed carbides of iron and nickel Fe_3C and Ni_3C , respectively. As might be expected these are thermally highly unstable, and decompose either to the metal and free carbon or to the more stable but more complex carbides such as the Hägg iron carbide and cementite. The complexity of the latter carbides is shown by their large lattice parameters, which are measures of the distance which must be traced through the crystal before the motif repeats itself.

Graphitic compounds. While not true carbides in the sense that no chemical bond of either the ionic or covalent type exists between the carbon and the other element, graphitic compounds should receive mention here. Graphite itself consists of sheets of catacondensed aromatic rings. Between these sheets potassium metal can intrude causing a swelling of the graphite in the direction perpendicular to the sheets. The bonding between the carbon and the potassium is of Van der Waals type. The graphite can be regenerated by distilling off the potassium. Graphite is known to form other similar interlayer compounds with other reagents.

L. J. E. HOFFER

Cross-references: Carbon (*Industrial*), Carbon Monoxide, Carbon Dioxide, Acetylene Refractories

Industrial Metallic Carbides

Refractory carbides. These are characterized by great chemical and thermal stability. They include the carbides of boron and silicon together with the carbides of the transition metals. The latter are interstitial compounds in which the carbon atoms fit into interstices of the normal

crystal lattice of the metal. Such compounds exist only in the solid state. Ordinary valence considerations are not involved, the composition depending upon the geometry of the system. When the ratio of the carbon atom radius to that of the metal atom is below 0.59, the carbide has a simple, close-packed structure and a one-to-one atomic ratio. More complex structures of lesser stability are formed with transition metals of smaller atomic size.

Metals which form interstitial carbides of simple MC type are titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, and tungsten. These carbides are generally grey, metallic-appearing powders which conduct electricity. They are extremely hard and high-melting. Except for the similar interstitial borides, they are the only known substances which are stable solids at 2500°C in vacuo. Tantalum carbide has the highest melting point known, 3880°C.

Carbides of the M_3C type, in which only half the interstitial positions are occupied, are also known for several of these metals. Phase relations for the metal-carbon systems are complicated by solid state solubility of both carbon and metal in the carbide phases. Solid state solution of carbon in metal without formation of a carbide phase also occurs. In general, these compounds exist over a range of compositions, and samples of exact stoichiometric composition are rarely obtained.

While relatively inert chemically, the carbides are decomposed by fusion with alkalis, and many are attacked by mixtures of nitric and hydrofluoric acids. They are readily oxidized or chlorinated at high temperatures.

The transition elements of smaller atomic volume form an intermediate series of interstitial carbides. Chromium forms several carbides of which Cr_3C_2 is most stable. Manganese, iron, cobalt, and nickel form carbides of the M_3C type. Mn_3C is hydrolyzed to give a mixture of hydrocarbons, while the others are decomposed by hydrochloric acid giving a mixture of carbon and hydrocarbons. These carbides are softer and less refractory than those of the MC type. The carbides of iron, cobalt, and nickel are thermodynamically unstable and decompose to the metal and carbon on long heating.

The carbides are prepared in pure state by heating intimate mixtures of carbon and metal at temperatures up to 2500°C in a vacuum or inert atmosphere. Considerable time may be required to complete the slow diffusion of carbon into the solid metal. The metal may be generated *in situ* by the reduction of its oxide or other compound by excess carbon. Similarly, carbon may be introduced to the reaction zone in the form of a hydrocarbon. Electric furnace temperatures are generally required.

Carbides can be synthesized at lower temperatures in a menstruum of molten metal and then recovered by dissolving the excess metal in acid. Thus Fe_3C is produced as a black, finely powdered residue by dissolving cast iron in nitric acid. Tempered tungsten steels may give a quantitative yield of tungsten carbide when dissolved in sulfuric acid. The menstruum process can be adapted to aluminothermic methods. The metal oxide is

reduced by excess aluminum in the presence of carbon. The excess aluminum is then dissolved away by acid treatment. Silicon carbide ("Carborundum"), boron carbide, and titanium carbide were discussed in the first section of this article.

Cemented carbides. Cutting edges of tools and other wear-resistant parts of great strength and hardness are produced by alloying carbides with small amounts of binding metals. Powder metallurgy techniques are used. "Carboly" is the tungsten carbide composition with 5% of cobalt binder. The finely powdered mixture is formed to shape in steel dies at pressures of 10 tons to the square inch. The compacts are then sintered in vacuum or a hydrogen atmosphere at 1450°C. Mixtures of tungsten and titanium carbides are also used with the cobalt binder. The carbides must be of high purity since oxides or free carbon prevent alloying with the cobalt.

Carbides are important constituents in the ceramic-metal compositions (cermets), which possess unusual high temperature strength and corrosion resistance. Experimental gas turbine blades have been fabricated from titanium carbide and silicon.

Metallurgy. Blast-furnace production of iron is possible because the eutectic composition of iron carbide and iron is liquid at attainable temperatures. Molten cast iron contains 60 to 65% of dissolved Fe_3C . On solidifying, the carbide partially crystallizes as *cementite* (Fe_3C) and partially decomposes to iron (*ferrite*) and graphite. Steel contains less than 25% of Fe_3C alloyed with iron. In this range, a solid solution of carbide and gamma iron forms on solidification. The *austenite* solid solution phase is not stable below 723°C, but decomposes to ferrite and cementite. However, rapid chilling (*tempering*) may partially preserve the austenite structure. Hardness increases with increasing carbon content.

The transition metals alloy with steel to alter the equilibrium relations of the iron-carbon system. Manganese and vanadium improve the hardenability of steel while chromium, in the low-carbon stainless steels, preserves the corrosion-resistant austenite structure. These elements form more stable carbides than iron and so prevent the crystallization of a cementite phase. Tungsten tool steels have much of the hardness and wear resistant properties of tungsten carbide. Alloy steels may be considered alloys of iron with the carbides of other transition metals.

INDUSTRIAL CARBIDES

Carbide	% Carbon	m.p., °C	Density
B_4C	21.72	2350	2.52
CaC_2	37.47	2300	2.16
SiC	29.97	2700 (subl.)	3.22
TiC	20.03	3140	4.97
NbC	11.45	3500	7.82
Cr_3C_2	13.33	1860	6.68
TaC	6.23	3880	14.48
WC	6.13	2860	15.7
Mo_2C	5.89	2600	8.9

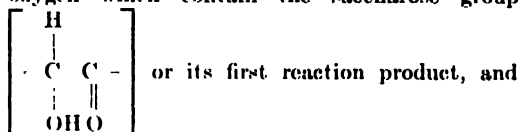
MEYER I. FREEDMAN

Cross-references: Acetylene, Carbon, Refractories

CARBOHYDRATES

Carbohydrates are the most abundant class of organic compounds. They constitute three-fourths of the dry weight of the plant world and are widely distributed, often as important physiological components, in animals and lower forms of life. In plants and animals they serve mainly as structural elements or as food reserves. Plant carbohydrates, in particular, represent a great storehouse of energy either as food for men and animals, or after transformation in the geological past as coal and peat. Large industries process such carbohydrates as sucrose, starch, cellulose, pectin and certain seaweed polysaccharides.

The term carbohydrate originated from the belief that this class of compounds consisted of hydrates of carbon because elemental analysis of common carbohydrates, such as lactose, sucrose, starch and cellulose, led to the empirical formula $\text{C}_x(\text{H}_2\text{O})_y$. Although the formula represents the majority of carbohydrates, many have compositions which do not fit such a simplified generalization. While it is not possible to give a simple yet comprehensive definition of such a broad group of compounds, one fairly good definition describes them as compounds of carbon, hydrogen and oxygen which contain the saccharose group



which usually have the hydrogen and oxygen in the ratio found in water.

Most carbohydrates are hydroxyaldehydes or hydroxyketones or substances producing them by hydrolysis. Glyceraldehyde (HOCH_2CHO) is considered the simplest carbohydrate, but glyceraldehyde, (glycerose, $\text{HOCH}_2\text{-CHOH-CHO}$), is more representative because it contains an asymmetric carbon atom and is optically active. All other aldehydic carbohydrates contain one or more asymmetric carbon atoms and influence a beam of polarized light according to the rules of stereochemistry. Because glycerose contains an aldehyde group it is classified as an *aldose*. Since it contains three carbon atoms it is an *aldotriose*. There are similar aldose molecules with three, four, five or more alcohol groups for each aldehyde group. Such molecules have four, five and six or more carbon atoms respectively and are therefore aldotetroses, aldopentoses, aldohexoses, etc. Common aldopentoses are xylose and arabinose while common aldohexoses are glucose, mannose and galactose. Another group of carbohydrates are ketones with dihydroxyacetone ($\text{HOCH}_2\text{-CO-CH}_2\text{OH}$) as the simplest member. These substances are *ketoses*. Dihydroxyacetone is a ketotriose. There are also ketotetroses, ketopentoses, ketohexoses and higher members. All these, except the ketotriose, contain asymmetric carbon atoms and are optically active. Common ketohexoses are fructose and sorbose.

All the above carbohydrates contain one saccharose group and are classified as *monosaccharides*. More complex carbohydrates that break up

on hydrolysis to produce two monosaccharides are called *disaccharides*. Still larger carbohydrates are classified, depending on the number of monosaccharides each molecule produces, as *trisaccharides*, *tetrasaccharides*, and so on. *Oligosaccharides* is a collective term given to carbohydrates which contain two to ten monosaccharide units. All carbohydrates which contain more than ten monosaccharide units are classed as *polysaccharides*; typical examples are starch, pectin, glycogen and cellulose.

All the monosaccharides and many of the oligosaccharides are called *sugars*. Frequently the monosaccharides are called "simple" sugars. The sugars are readily soluble in water but vary greatly in their sweetness. The sweetest, fructose, is about 1.5 times as sweet as sucrose (table sugar) and about 3 times as sweet as glucose (corn sugar). Other sugars are less sweet, with some exhibiting a barely noticeable sweetness.

When the sugar structural formulae are written in the vertical position with the aldehyde (or ketone) function at the top, half will have the hydroxyl group next to the primary alcohol group lying on the right side of the molecule as with dextrorotatory glycerose, and half will have this penultimate hydroxyl group lying on the left as in levorotatory glycerose. The former are therefore classified to the *D* series and the latter classified as *L*-series. It should be understood that these symbols denote configurational relations only and do not indicate the optical rotation of the molecule.

Because of the presence of asymmetric carbon atoms, numerous stereoisomeric monosaccharides exist. Although the structures of carbohydrates are often written as acyclic compounds, they usually occur as cyclic compounds formed by the carbonyl group condensing with the hydroxyl group on carbon C_4 or C_5 . These forms are designated as furanose and pyranose, respectively. Because of the cyclization, carbon atom C1 is an asymmetric center which gives rise to two anomers. When the hydroxyl group of the anomeric carbon atom is in the same direction as the penultimate hydroxyl group the sugar is designated as the α -form. On the other hand, when the hydroxyl group is in the opposite direction the sugar is the β -form. All these forms, together with the acyclic form, coexist in an equilibrated, aqueous sugar solution.

Monosaccharides. The aldotrioses, *D* glyceraldehyde, and dihydroxyacetone are very important biochemically since they occur as integral parts of the glycolytic cycle of carbohydrate metabolism in both plants and animals. None of the aldotetroses, *D*- or *L*-threose or *D*- or *L*-erythrose is common or of much importance.

D-Xylose is rarely found free in nature but is abundant as units in the polysaccharide xylan found in various plants. It is freed by subjecting corn cobs or seed brans to hydrolysis by hot dilute mineral acid. Concentration of the hydrolyzate and purification with carbon causes the sugar to crystallize. Subjecting corn cobs, brans or other plant tissues high in xylan content to hot 12% HCl causes conversion of the *D*-xylose and some other substances (glycuronic acids) to *furfural*. The

process can be used for quantitatively measuring the amounts present of pentose containing polysaccharides (pentosans). It is also used commercially for manufacture of *furfural*.

L-Arabinose occurs in nature, sometimes in polysaccharides combined with *D*-xylose units but more often in polysaccharide gums and as a polysaccharide component of pectin. It may be prepared by mild acid hydrolysis of such plant gums as mesquite, arabic or cherry. *D*-Arabinose does not occur in nature but may be prepared by appropriate degradation of *D* glucose. *D*-Ribose is an important constituent of nucleic acids which are found in all plant and animal cells. Ribonucleic acids are usually found in the cytoplasm whereas 2-*D*-deoxyribose nucleic acids are found in the nucleus. 2-*D*-Deoxyribose has the hydroxyl group on carbon atom C2 replaced with a hydrogen atom. Lyxose does not occur in nature.

D-Glucose is the most abundant and important of the aldohexoses. It occurs free in fruits, plant juices, honey lymph, cerebrospinal fluid, urine and blood. Normal human blood contains 70 to 100 mg. of *D*-glucose per 100 ml. *D*-Glucose is taken into the blood from the intestines as a result of digestion of sucrose, starch and other carbohydrates. It is delivered to the body cells and muscles to supply energy through enzymatic glycolysis and the citric acid cycle. Solutions of *D* glucose are sometimes used for intravenous feeding of hospital patients. The sugar is produced commercially in large amounts by hydrolysis of corn starch. It is crystallized and sold as "dextrose" but the largest amount is sold in solution as corn sirup. For this purpose the hydrolysis of the starch is stopped short of completion so that the hydrolyzate contains besides *D* glucose various oligosaccharide fragments, resulting from incomplete depolymerization of the starch molecules. Their presence in the sirup prevents crystallization of the *D*-glucose and hence promotes sirup stability. *D* Glucose is also a constituent of sucrose (table sugar).

D-Galactose is a constituent of the disaccharide lactose, from which it may be prepared by hydrolysis. The sugar may also be obtained in good yield by hydrolysis of numerous polysaccharides which contain *D*-galactose in varying amounts. Some such as agar and carrageenan are composed almost entirely of *D*-galactose units. From such polysaccharides *L*-galactose may sometimes be obtained in small amounts.

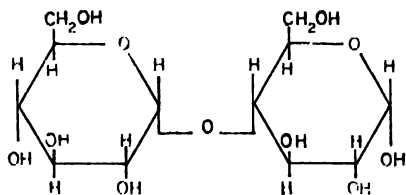
D-Mannose is widely distributed in nature as a repeating unit in polysaccharides known as mannans.

Among the ketohexoses *D* fructose (levulose) is most abundant and important. It occurs with *D*-glucose in honey and in "invert sugar" which is the product of sucrose hydrolysis. Sucrose is dextrorotatory and the hydrolyzed mixture is levorotatory; hence the name *invert sugar*. *D*-Fructose can be separated from invert sugar, but in the laboratory it is made by hydrolysis of one of its numerous polymers, polysaccharides termed fructans which are commonly found in plants as reserve foods. Inulin from dahlia tubers is a convenient source. *L*-Sorbitol, an intermediate in the

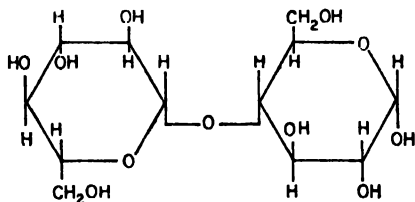
synthesis of ascorbic acid (vitamin C), is prepared by the bacterial oxidation of sorbitol.

Of the four naturally occurring "methylpentoses" or 5-C-methylaldopentoses, L-rhamnose or 6-deoxy-L-mannose is the commonest. It is obtained by hydrolysis of quercitrin.

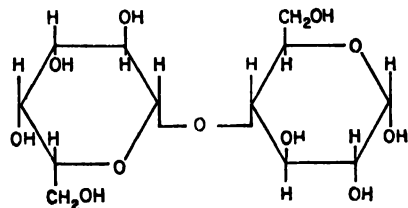
Disaccharides. Disaccharides are formed by condensation of two monosaccharides through one or both of the carbonyl groups. The new linkage is labile to acid and often to alkali. Acid hydrolyzes the disaccharide to its constituent monosaccharides. Disaccharides which have a free carbonyl group show reducing properties. The more important members of this group are maltose, cellobiose and lactose. Maltose is readily prepared by the



Maltose



Cellobiose

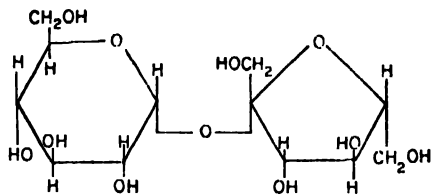


Lactose

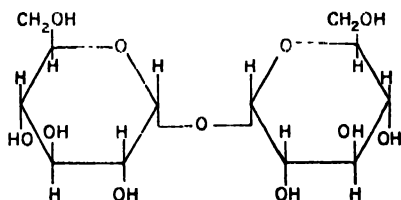
partial acid or enzymatic (diastase) hydrolysis of starch. Cellobiose is obtained by the partial acid hydrolysis or acetyolysis of cellulose, whereas lactose, sometimes called milk sugar, is usually obtained by evaporation of whey whereby crystalline lactose is deposited.

Those disaccharides in which both of the carbonyl groups are involved in the linkage have only slight reducing properties. The two most important nonreducing disaccharides are sucrose and trehalose. *Sucrose* is obtained commercially from sugar cane or sugar beet. The sucrose is extracted by crushing and extraction with water. Purification is by heating the extract with calcium hydroxide which causes the impurities to separate either as a scum or a deposit. Concentration of the clear solution yields crystalline "raw" sugar. Table sugar is obtained by recrystallization of the raw sugar. The mother liquors from this process deposit less pure crystals known as "brown"

sugar. α,α -Trehalose is found in rye ergot and young mushrooms, but the best sources for its isolation are trehala manna, an exudant of certain insects found in Syria, and the *Selaginella Cepidophylla* plant of southwestern United States.



Sucrose

 α,α -Trehalose

Oligosaccharides. The commonest oligosaccharides found in nature are derivatives of sucrose.

Polysaccharides. The polysaccharides are widely distributed in the plant and animal worlds, serving as food reserve substances and structural material. The two best known polysaccharides are starch and cellulose, which consist of D-glucopyranosyl units linked by α - and β -1 \rightarrow 4 bonds, respectively. Similar to cellulose is xylan, a polysaccharide consisting of β -1 \rightarrow 4 linked D-xylopyranosyl units. This polysaccharide occurs in practically all land plants and in some marine algae. Although xylan is difficult to extract from cellulose, there is no positive evidence for covalent linkages between the two polysaccharides.

Also similar in many ways to cellulose is *chitin*, the most abundant of the polysaccharides containing aminosugars. It is the principal structural component of the shells of insects, crabs, and lobsters, and is also found in lower plants such as the mycelia and spores of fungi.

Polysaccharides may also be built of uronic acid units. For instance alginic acid, a constituent of the cell walls of most brown algae, is a linear polymer made up entirely of D-mannuronic acid units united by β -1 \rightarrow 4 linkages. The presence of the uronic acid group stabilizes the glycosidic linkage to acid hydrolysis. Treatment with 19% hydrochloric acid at 145° for 2 hours causes decarboxylation and the theoretical amount of carbon dioxide is evolved. During the last decade alginic acid has become an important commercial product and is used extensively in the food industry. Since the calcium salt of alginic acid can form strong fibers which are soluble in mild alkali, it is used in the textile industry for weaving special fabrics such as imitation lace and furs. The alginic acid fibers are used as a frame-work during weaving and then are dissolved out by alkali.

Certain polysaccharides occur as esters of sul-

furic acid. Two such polysaccharides are agar and carrageenan, β -1 \rightarrow D-galactans with sulfate groups at certain C₄ and C₆ hydroxyl groups, respectively. Both polysaccharides, which are isolated from red marine algae, form reversible gels in aqueous solution. Because of this property they are used as stabilizers and gels in the food industry.

Reactions of Carbohydrates. Carbohydrates which contain a free carbonyl group have reducing properties typical of those of the simple aldehydes. The carbonyl group will also undergo condensation with amines, hydrazines, mercaptals and hydrogen cyanide to form derivatives which are useful for identification. Aldehyde groups are quantitatively oxidized to a carboxyl group by bromine or alkaline iodine. This reaction is used extensively for the determination of aldoses in the presence of ketoses and for molecular weight determinations. Carbonyl groups may also be reduced to alcohols.

The polyhydric nature of the carbohydrates is illustrated by the formation of esters and ethers. Esters of carbohydrates are usually prepared by the action of inorganic acids, organic acids or anhydrides of the latter in the presence of an impelling agent such as sulfuric acid, phosphoric acid or pyridine. The presence of ester groups reduces the solubility of the carbohydrate in water but increases the solubility in organic solvents. Carbohydrate ethers are usually prepared by the action of alkyl halides or sulfates on a sodium hydroxide dispersion of the carbohydrates. Complete etherification is achieved only after repeated treatment. The ethers and esters of polysaccharides, especially of cellulose and starch, are of fundamental commercial importance.

Hydroxyl groups of carbohydrates are readily oxidized to acids, aldehydes and ketones. The mechanism of oxidation is quite complex and only with lead tetracetate and periodic acid is the reaction specific. In these cases vicinal hydroxyl groups (α -glycol groups) are cleaved to give carbonyl groups. Glycol groups containing a primary alcohol group give rise to formaldehyde whereas three vicinal secondary hydroxyl groups give formic acid. α -Hydroxycarboxylic acids react slower and produce carbon dioxide. The quantitative study of lead tetracetate and periodate oxidation of carbohydrates is most valuable in structural determinations. Hypochlorite and hydrogen peroxide are used commercially for modifying the properties of polysaccharides such as starch. The mechanism of oxidation and the type of products produced are still unknown. A general characteristic of oxidized carbohydrates is their sensitivity to alkali.

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Cross-references: *Asymmetry, Sugars, Cellulose, Starches, Foods, Nutrition*

CARBON, ACTIVATED

Activated carbon is a manufactured form of carbon having a large specific area and designed for adsorption from either the gas or liquid state. It is made by destructive distillation of carbonaceous material under controlled conditions. The specific area of an activated carbon may range from 600 to 2,000 square meters per gram. In both granular and powdered carbons, this area is almost entirely internal; it is the area of the pore structure created by the two steps of driving off volatile constituents from the carbonaceous raw materials, and oxidizing the residue. Such oxidation is accomplished by means of steam or carbon dioxide, at temperatures approximating 1000°C.

Carbons activated for adsorption of gases and vapors differ markedly from those designed for adsorption from liquids. The former class is characterized by a preponderance of small pores (under 20Å in diameter); they are in general harder and denser than the so-called "decolorizing" carbons. The fine pore structure required for gas-adsorbent carbon may be secured either by choice of suitable raw material or (within limits) by choice of the method of manufacture. Coconut and other nut shells are ideal raw materials for producing such carbons.

The "decolorizing" carbons for liquid phase use (which adsorb many noncolored substances as well) are divided into the animal and vegetable carbons. The former, and historically older, type is made from animal bones. The finished bone char ranges approximately 12 by 20 mesh, and consists of about 90+% of hydroxy apatite, the balance being carbon. The vegetable-activated carbons of commerce are made from lignite, paper mill waste liquor (i.e., lignin), peat, and wood. They are sold mostly in powdered form. Activated carbons of both the gas-adsorbent and decolorizing types can also be made by chemical activation. Here the pore structure is initiated by destructive dehydration instead of destructive distillation. The agents used are zinc chloride, phosphoric acid, or sulfuric acid.

Activated carbons are usually leached to extract inorganic contaminants, if they are to be used for purifying food or chemical products. Such leaching is done with mineral acid, and is followed by water washing to eliminate excess acid and salts. A good grade of activated carbon as sold will contain well under 1% of soluble impurity.

The military use of the gas-adsorbent carbons in gas masks is well known. There are a number of sizable peace-time uses as well. Important among these is the recovery of volatile solvents in industrial processes. Air or gas streams containing such solvent vapors, even in very low concentrations, are effectively stripped by passage through a bed of granular gas-adsorbent carbon. After a suitable adsorption period, the solvent is desorbed, usually with steam, and recovered by conventional condensation.

The same principle is used, but at higher concentration levels, in the petroleum industry for separation of hydrocarbons by fractional adsorption.

CARBON, see ORGANIC CHEMISTRY; CHEMICAL DATING; CARBON BLACK; ALLOTROPES; CARBON, ACTIVATED; CARBON, INDUSTRIAL

This is useful with lower members of the aliphatic series, where low boiling points cause complications in separation by distilling and subsequent condensation.

Other applications of gas-adsorbent carbon include the removal of oil vapor, sulfur compounds and other contaminating agents from such industrial gases as carbon dioxide, carbon monoxide, hydrogen and acetylene. Objectionable odors or irritating vapors are removed from air to be circulated in theaters, restaurants, offices, railroad cars, airplanes, and other places for human comfort. Both gas-adsorbent and decolorizing carbons are used as catalysts or catalyst carriers for various commercial organic chemical reactions such as hydrogenation and synthesis of vinyl chloride.

The "decolorizing" carbons, both animal and vegetable, find a major use in the refining of raw cane sugar. Bone char dates back well into the nineteenth century. It is used in large char towers through which sugar liquor is percolated for removal of color as well as inorganic constituents. The spent bone char, after "sweetening-off" with water to recover occluded sugar liquor, is regenerated by a heat treatment in char kilns; this process is very similar to the original activation. Some of the original carbon is burned off, but is replaced by secondary carbon from the organic nonsugars adsorbed in the char tower.

Powdered vegetable carbons are used for cane sugar refining in the tropics and have partially replaced bone char in U. S. refining. They have largely replaced bone char in the refining of corn syrup and corn sugar. The beet sugar industry in the United States also uses sizable tonnages of these carbons.

Another major field of use for the vegetable carbons is in the treatment of municipal water supplies. The objective here is the adsorption of impurities producing odor and taste. These may arise from industrial pollution, from decay of vegetation, or from algae. The carbon is applied in powdered form at the filtration plant, usually during the coagulation and sedimentation steps, in dosages averaging only two to five parts per million. These low levels are effective because the odors and tastes are caused by such minute concentrations of organic compounds.

A similar function is performed by granular activated carbon on industrial water supplies. In the soft drink and brewing industries taste-free and substantially sterile water is essential; sterilization is effected by heavy chlorine treatment. Carbon is used to remove residual chlorine, as well as odors and tastes, in a single operation. Other large fields of use for the vegetable carbons are the treatment of glyceride-type oils and fats, waxes, plasticizers and other esters, the purification of nylon monomer, polyhydric alcohols such as glycerine, the glycols, pentaerythritol and sorbitol; food products such as gelatin, pectin, vinegar, and monosodium glutamate; photographic chemicals and pharmaceuticals such as sulfa drugs, antibiotics, blood plasma extenders and synthetic vitamins; organic acids including

acetic, benzoic, citric, fumaric, maleic, and many others; natural and synthetic caffeine, dye intermediates, and a great host of miscellaneous products.

In recent years two other large-scale uses have developed for activated carbon. One of these is the immobilization of a troublesome liquid in an essentially solid-phase system. When reclaimed rubber is used in the production of white side-wall tires or other light colored rubber products, some of the oils used in the reclaiming process tend to migrate from the back ply to the light outside ply and cause a yellow stain. When activated carbon is milled with the reclaimed rubber, these oils are immobilized on the carbon and staining is prevented.

The other is the use of carbon to adsorb impurities causing haze in a liquid product on long storage or on chilling. This may be the case with some types of sugar used in the soft drink industry, and in the past it has also caused much concern in the brewing industry. Such haze is caused by the presence of an impurity at or near the point of insolubility; substances like this are readily adsorbed. Activated carbon is thus becoming a valuable aid to the brewing industry where it supplements the enzymes employed to offset chill haze caused by protein precipitation.

Some proprietary names in this country are: Adsorbite, Aqua Nuchar, Bone Char, Carbox, Carbo-Dur, Cliffchar, Columbia Activated Carbons, Darco Activated Carbons, Dehydrite, Deodorite, Filtechar, Girdler Charcoal, Granular Hydrodarco, H-VW-M Activated Carbon, Minchar, Norit, Nuchar, Pittsburgh Activated Carbons, Suchar and Synthad.

WALTER A. HELBIG

Cross-references: Absorbents, Adsorption, Brewing, Sugar, Chemical Warfare

CARBONATES

The carbonates are of considerable industrial importance. The largest tonnages are consumed in the ceramic and metallurgical industries. For example, limestone (essentially CaCO_3) as a source of CaO , is used extensively for fluxing and refining purposes in iron and steel making. CaO , derived from CaCO_3 in sea shells, is used for the recovery of Mg from sea water. Dolomite [$(\text{CaMg})(\text{CO}_3)_2$] and magnesite (MgCO_3) as sources of MgO , are used for the manufacture of refractories. Limestone, as a source of CO_2 , is used in the Solvay process for the manufacture of Na_2CO_3 and NaHCO_3 . Thus, both products of decomposition of abundant limestone are important. Na_2CO_3 , as a source of Na_2O , is used for the manufacture of glass.

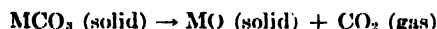
Most metals form carbonates, and a great many of these are found native. The metals which do not form carbonates are those whose hydroxides are very weak bases, for example Al and Cr . The carbonates can be classified as ionic compounds. The carbonate ion is planar and since the three $\text{C}-\text{O}$ distances are equal, it is believed that reso-

nance of a double bond occurs among the three C—O positions.

Metal carbonates are very slightly soluble in water, those of the alkali metals and Ti_2CO_3 being the only important exceptions. Therefore, the metallic carbonates can usually be prepared by precipitation by the action of a solution of a carbonate on a solution of a soluble salt of the metal. $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 are also soluble in water at room temperature but decompose in hot water. The action of excess CO_2 on carbonates in solution results in the formation of bicarbonates, which are more soluble. "Temporary hard water" contains bicarbonates in solution which decompose on heating to form the less soluble carbonates. The latter carbonates precipitate out of solution and yield the deposit often observed on the walls of teakettles and boiler pipes. Carbonates are decomposed by acids with evolution of CO_2 . CO_2 is slightly soluble in H_2O , and this solution exhibits feeble acid properties. It contains carbonic acid, H_2CO_3 , which is unstable and cannot be isolated.

The thermal decomposition rates of the carbonates increase with increasing temperature. For some, rapid decomposition starts at comparatively low temperatures (Ag_2CO_3 , 200°C , for example) whereas for others, rapid decomposition starts at comparatively high temperatures (CaCO_3 , 880°C , for example). In addition, the alkali metal carbonates melt before rapid decomposition occurs.

There exists at a given temperature a minimum pressure or partial pressure of CO_2 in the environment which will prevent a carbonate from decomposing. This pressure is known as the equilibrium decomposition pressure for the carbonate, and it increases with increasing temperature. At a given temperature, this pressure is different for the various carbonates existing in nature. The above statements can be placed on a thermodynamic foundation by considering the thermal decomposition of the carbonate MCO_3 , where M is a bivalent metal cation. The decomposition reaction is:



The equilibrium constant, K , for this reaction is $(P_{\text{CO}_2})_e$, where $(P_{\text{CO}_2})_e$ is the equilibrium partial pressure of CO_2 . The activities of MO and MCO_3 are unity, since they are in their standard states. Thus, the free-energy change for this reaction is

$$\begin{aligned}\Delta G &= -RT \ln (P_{\text{CO}_2})_e + RT \ln P_{\text{CO}_2} \\ &= \Delta G^\circ + RT \ln P_{\text{CO}_2}\end{aligned}$$

where R is the gas constant, ΔG° is the standard free-energy change, and P_{CO_2} is the partial pressure of CO_2 in the environment at a given absolute temperature T . When $P_{\text{CO}_2} = (P_{\text{CO}_2})_e$, this reaction is at equilibrium or no net change occurs and $\Delta G = 0$. When

$$P_{\text{CO}_2} < (P_{\text{CO}_2})_e$$

ΔG is negative and the reaction proceeds continually to the right provided this condition is maintained. When

$$P_{\text{CO}_2} > (P_{\text{CO}_2})_e$$

ΔG is positive and no decomposition can occur. In fact, if free MO is present under this latter condition, it will convert to MCO_3 . Therefore, the driving force or tendency for decomposition to occur is determined by the equilibrium partial pressure of CO_2 , analogous to the use of vapor pressures of substances as an indication of their vaporizing or escaping tendency.

The equilibrium partial pressure of CO_2 for CaCO_3 at 880°C is one atmosphere, whereas for Li_2CO_3 , Na_2CO_3 and K_2CO_3 at 1200°C , the equilibrium partial pressures in mm Hg are 300, 41, and 27, respectively. The melting points of the latter three carbonates are 618, 851, and 890°C , respectively. CaCO_3 melts below 1100°C if the CO_2 pressure in the environment is maintained above the equilibrium decomposition pressure. It is apparent that the atomic binding forces are different in the various carbonates.

An equilibrium decomposition temperature is ascribed to the various carbonates. It is the temperature at which the P_{CO_2} required for equilibrium is one atmosphere. In this case, the standard free-energy change, ΔG° , is also zero. For the carbonates of Mg, Ca, Sr, and Ba, the equilibrium decomposition temperature increases with increasing atomic number of the cation or with increasing cation radius. The heat of decomposition can be obtained by measuring the equilibrium decomposition pressure as a function of temperature and utilizing the Gibbs-Helmholtz equation. The equilibrium partial pressure or ΔG° for a given temperature can also be calculated from thermochemical data provided the solid reactants and products are at unit activity or if activity data are also known.

The decomposition of a carbonate particle starts at the surface and proceeds inward. It is known that the zone of decomposition increases linearly at a given temperature for CaCO_3 , MgCO_3 , $(\text{CaMg})(\text{CO}_3)_2$, and (Ag_2CO_3) . This rate of zone increase is constant at a given temperature regardless of the diameter of the particle. It appears, at least for these carbonates, diffusion of CO_2 from the decomposing interface is not the limiting process. Any mechanism of decomposition must include the above observation and the fact that the resulting oxide usually has a different crystal structure than the parent carbonate. The overall process can be represented by two consecutive reactions: The first, decomposition; and the second, a phase change.

The thermal decomposition rate of the carbonates can be increased by the presence of other gases in the environment, notably H_2O and NH_3 . These gases have large dipole moments in the liquid state and are dipoles in the gaseous state and can catalyze the decomposition.

J. H. WERNICK

Cross-references: *Thermodynamics*

CARBON BLACK

Carbon black is the generic name for a group of intensely black, submicron size pigments composed of essentially pure carbon and made by

vapor phase decomposition of hydrocarbons in an open diffusion flame, in a partial combustion chamber or in a thermal decomposition chamber in absence of air. Common soot is a true carbon black; commercial carbon blacks are the result of making soot under exactly controlled process conditions.

The following commercial products are classed as carbon blacks: channel black (also called impingement black), furnace black, lampblack, acetylene black and thermal black. In 1951 the U. S. produced about 110 million dollars worth of these products, or 1.6 billion pounds, which amounted to 80-85% of the world's supply of black.

Carbon black is formed in a fraction of a second in a flame having a mass temperature ranging from about 2100 to 2700°F; at this temperature level all hydrocarbons decompose rapidly to molecular fragments which in turn condense or polymerize to polynuclear aromatics. These aromatic "compounds" grow rapidly and dehydrogenate almost completely by the time the final carbon particle is formed. Evidently nuclei, which have never been isolated and identified, are formed by *thermal degradation of the hydrocarbon raw material*. The nuclei grow almost instantaneously into the final carbon particles which, in turn, have a tendency to aggregate. The 3 dimensional branched aggregates are held together with varying degrees of bond strength, known as "structure", depending on fuel and production conditions.

X-ray analysis indicates that all carbon blacks are made up of crystallites containing parallel layer groups similar to graphite except that the layers are randomly oriented about the layer normal and the layer spacing is slightly greater than in graphite. Prolonged heating at 2700-3000°C rapidly graphitizes carbon black with considerable growth in crystallite size.

The range of mean particle size of commercial carbon blacks is from about 10 to 500 m μ with the distribution about the mean usually broadening as particle size increases. Channel blacks may contain up to about 11% oxygen and 0.8% hydrogen; oxygen contents above about 4% are usually obtained only by secondary aftertreatment in an oxygen-containing atmosphere at 800-1000°F or by prolonged high temperature exposure on the channels. Channel blacks contain negligible amounts of benzene soluble matter; ash is usually 0.10% or less.

Furnace and thermal blacks contain about 0.3-0.5% each of hydrogen and oxygen, a trace of benzene extractables up to a maximum of a few tenths of a percent and ash contents of 0.1 to 1.5% depending upon the solids content of the water used in cooling. Sulfur content of black depends on sulfur content of the fuel; in commercial furnace blacks sulfur varies from 0.1 to 1.5%. Neither sulfur nor ash have important primary effects in carbon black applications but oxygen content (or some variable related to oxygen content) has a strong influence on the dispersing properties of blacks in fluid systems.

The pH of aqueous suspensions of ash-free carbon black varies from about 3.0 for aftertreated

channel blacks to 7.0 for furnace black as oxygen content varies from 11% to under 0.5%. In practice furnace blacks are alkaline (up to pH 10) due to contaminants from cooling water.

The most important present day commercial carbon black process is the so-called furnace process. This involves non-pre mix partial combustion of atomized liquid or vaporized hydrocarbon fuels, with natural, refinery or coke oven gas as auxiliary fuels, and with air as an oxygen source in a refractory enclosure or furnace. Black is collected from the smoke by electrostatic agglomeration followed by cyclone collection; in recently built plants bag filters or wet scrubbers are used to remove the last traces of carbon.

The channel black process, in use since about 1880 and intensively developed in the period 1920-30, is still widely used, accounting for about 27% of U. S. output in 1954. Before 1940 channel black constituted over 90% of the world's supply of carbon black. In this process small flat non-aerated flames are played against an air-cooled steel channel about 10 inches wide and up to 140 feet long. The channel, which serves as a collector, is moved slowly past fixed scrapers which discharge the black into hoppers feeding screw conveyors. Collected yield is 2-6% of the total carbon in the gas depending upon the particular quality of black being made.

In the thermal black process natural gas is decomposed or "cracked" by contact with hot silica checker brick in a cyclic process employing 2 chambers alternately used on heating and cracking cycles. Collection of black from the gas stream is usually by bag filters with or without cyclones in series. Net yields are in the range of 25-40% when the by-product hydrogen is used as heating fuel. U. S. thermal black production in 1951 was about 8% of total carbon black production.

The lampblack process is a crude form of furnace process in which a pan of oil is burned in a restricted updraft; the black passes into gravity settling chambers and, in more modern plants, the residual black is collected by bag filters or electrostatic precipitators. In the U. S. lampblack is used mainly for tinting paints and in liquid oxygen explosives. Lampblacks are rapidly becoming obsolete and will probably almost disappear in the U. S. in 5 to 10 years but perhaps will be used longer in Europe.

Acetylene black is made by exothermic decomposition of nearly pure acetylene in a refractory chamber; yields are practically 100%. This very high structure black is used almost exclusively in dry cell batteries and in making electrically conductive rubber and conductive dispersions in general. None is produced in the U. S.; Canada produces most of the world's supply. In 5 or 10 years acetylene black may be supplanted by special grades of oil furnace blacks. This has already occurred in the conductive rubber field. World production of acetylene black in 1954 was of the order 20-25 million pounds; Canada produced about 15 million pounds half of which was imported by U. S. customers.

Production of carbon black outside the U. S. is growing rapidly with important plants in Ger-

many, England and Canada. All new plants and expansions are oil furnace blacks. Foreign production, excluding U. S. S. R., was about 200 million pounds in 1954. It is estimated that Russia and satellites currently produce 50-100 million pounds yearly and this figure will increase rapidly.

Particle Size

Over 90% of all carbon black produced is used in natural and synthetic rubber as a reinforcing and filling agent; the largest single use is in motor vehicle and airplane tires. The most important variable affecting reinforcement is *particle size*; in general, basic reinforcing properties—tear resistance, tensile strength, and abrasion resistance—increase as particle size decreases. Particle size is determined from electron microscope pictures in which only the outline or the external surface area is considered. Total surface area, which includes the area of pores and surface irregularities, is determined by nitrogen adsorption. The nitrogen adsorption surface areas of commercial blacks vary from 1 to 5 or 6 times that of the external area determined from electron microscope counts. Rubber grades of black have a ratio of nitrogen area to electron microscope area not over about 1.5. The higher the total surface area the slower the vulcanization rate, evidently due to greater adsorption of accelerators or intermediates formed in curing. Stiffening effects—modulus, viscosity, hardness—increase in proportion to structure and inversely with particle size. The mechanism of reinforcement of rubbers by black is not known.

Uses

The growth of the carbon black industry here and abroad parallels that of the rubber industry; for the U. S. an average growth rate of about 1% per year seems indicated as long as new competitive non-black fillers do not develop. For the rest of the world a growth in demand of 5 to 10% per year can be anticipated for the next 5 to 10 years.

About 90% of the blacks sold in the U. S. are in the price range 4.5 to 10.5¢/lb. f.o.b. plant, carload bags. Carbon black has a low specific gravity (1.86) compared to most filler pigments; its price is low in relation to its reinforcing power in rubbers. Synthetic white reinforcing fillers, principally silicates and hydrated silicas, are finding increasing use in rubber products where color, not reinforcement, is critical, e.g. in shoe soling. Clay and ground calcium carbonate, the cheapest non-black fillers, are not gaining in use relative to carbon black. It is difficult to see how carbon black, which is made from the heavier refinery fractions falling in the industrial fuel category, can be surpassed in reinforcing power per dollar by products made from chemical raw materials.

The second largest use of blacks is in inks, news ink accounting for most. Carbon black for use in black inks is not likely to be supplanted by other black pigments or dyes. The trend is towards methods of masterbatching black with vehicles to increase its density, reduce transportation costs, cut down dust and speed dispersion at the ink factory. Growth in ink use of blacks can be expected to follow the growth of newsprint, book

and magazine papers at 3 to 4% per year. The trend toward more color in newspaper advertising could slow the growth of black ink use.

Carbon blacks are also used in protective coatings, phonograph records, paper, carbon paper, concrete (coloring), plastics and synthetic fibers. Of these uses only the last two show prospects for significant growth. Polyethylene pipe and cable jacketing require black for ultraviolet protection. Rayon and other synthetic fibers can be made permanently black by incorporating black directly in the polymer solution or melt prior to spinning.

C. A. STOKES

Cross-references: Abrasion Resistance, Colloid Chemistry, Rubber

CARBON DIOXIDE

Industrial Aspects

Carbon dioxide, CO₂ or O=C=O, formula weight 44.01, is a colorless gas with a pungent odor and acid taste. The first recognition of carbon dioxide as a gas distinct from other gaseous substances is attributed to J. B. Van Helmont (1577-1644), who detected in the products of combustion of charcoal the same gas as that given off in the process of fermentation. Carbon dioxide is widely produced today as a by-product of fermentation and lime kiln operations and by separation from flue gases by absorption processes. Carbon dioxide is used in its liquid and solid as well as gaseous form in food preservation (dry ice), beverage carbonation, fire lighting, therapeutical work, mining operations, and chemical manufacture.

It occurs in the combustion products of all carbonaceous fuels and may be recovered from them in the various ways. It may also be obtained as a by-product of fermentation processes, limestone calcination, chemical synthesis involving carbon monoxide, reaction of sulfuric acid with dolomite, and from naturally occurring gases. Carbon dioxide is also a product of animal metabolism and is important in the life cycle of animal and vegetable matter on earth. It is thus present in the atmosphere in small quantities (about 0.03% by volume or 0.0474% by weight) but may not be recovered economically from this source, although the total available amount is about 2,750 billion tons.

The annual production in the United States of carbon dioxide, as obtained from the U. S. Department of Commerce, is given below (in thousands of pounds):

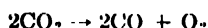
	1947	1949	1951	1953
Liquid	235,200	285,277	323,568	369,426
and gas				
Solid	720,401	818,272	964,924	1,117,310

Properties. Sublimation point, -78.5°C at atmospheric pressure; triple point, -56.6°C at 5.11 atmospheres (1 kg per cm²); critical temperature 31.0°C; critical pressure 72.80 atmospheres or 1070.16 p.s.i.a.; latent heat of vaporization 149.6 BTU per pound or 83.12 gm. cal per gm. at the triple point, and 101.03 BTU/lb at 0°C; gas

density, 1.976 grams per liter at 0°C and 1 atm; liquid density, 0.914 kg per liter at 0°C and 34.3 atmospheres; solid density, 1.512 kg. per liter or 94.39 lbs. per cubic foot at -56.6°C; solubility in water, 1.713 vols per vol. at 0°C and 0.759 vols. per vol at 25°C and 760 mm partial pressure of carbon dioxide. The heat of formation of carbon dioxide is 93.03 kg. cal per gram mol (or 167,454 BTU per lb. mol), showing the oxidation of carbon to be a highly exothermic reaction. Carbon dioxide will not support combustion and is used as a fire extinguishing agent.

Chemical Reactions. Carbon dioxide is not a chemically active compound as such and high temperatures are generally required to promote its reactions. In water solution, however, the opposite is the case as the solution is acidic in nature and many reactions take place readily. A few of the more important of these are included here.

Carbonic acid, H_2CO_3 , is formed by the reaction between water and carbon dioxide and is a highly dissociated acid. The pH of saturated carbon dioxide solutions in water varies from 3.7 at 1 atmosphere and 25°C to 3.2 at 23.4 atmospheres and 0°C. A hydrate, $\text{CO}_2 \cdot 8\text{H}_2\text{O}$, is formed on cooling at elevated pressures. CO_2 is generally stable and does not break down under normal conditions. At high temperatures the reaction

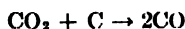


will take place. This reaction is also assisted by ultraviolet light, high pressure, and electric discharge but only a small percentage dissociation occurs.

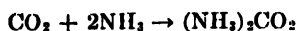
Carbon dioxide may be reduced by several means. The most common of these is the reaction with hydrogen:



This is the reverse of the "water gas shift" reaction which is used commercially in the production of hydrogen and ammonia. CO_2 may also be reduced catalytically with various hydrocarbons and with carbon itself at elevated temperatures. The latter reaction occurs in almost all cases of combustion of carbonaceous fuels and is generally employed as a method of producing carbon monoxide:



Carbon dioxide will react with ammonia, as in the first stage of urea manufacture, to form ammonium carbamate as follows:

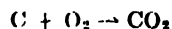


Carbon dioxide is an important factor in plant growth through the process of photosynthesis. This reaction takes place in the green coloring material in the leaves of plants and trees where the energy obtained by absorption from the rays of the sun causes a reduction of the carbon dioxide in the chlorophyll bearing cells to carbohydrates and oxygen. The oxygen is released to the atmosphere thus completing the carbon dioxide-oxygen cycle between animal and plant life.

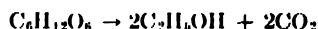
Commercial Production. Of the various sources the following are most important in the

commercial production of carbon dioxide:

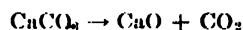
(1) Recovery from flue gases resulting from the combustion of carbonaceous materials according to the following formula:



(2) By-product of the fermentation industry in which a sugar such as dextrose is converted to ethyl alcohol and carbon dioxide by an enzyme reaction as follows:



(3) By-product of lime kiln operation in which naturally occurring carbonates are thermally decomposed according to this formula:



Although the carbon dioxide produced and recovered by the methods outlined above has a high percentage of purity, traces of hydrogen sulfide and sulfur dioxide are frequently present which gives the gas a slight odor or taste. The fermentation gas recovery processes include a purification stage but carbon dioxide recovered by other methods must be further purified before it is acceptable for beverage or dry ice use. This applies particularly to dry ice which is to be used for refrigerating food. The most commonly used purification methods are treatments with (1) potassium permanganate, (2) potassium dichromate, and (3) activated carbon.

Before the liquefaction of carbon dioxide, the water with which it has become saturated during the various recovery and purification operations must be removed. This may be accomplished by any one of several commercial methods such as treatment with calcium chloride, silica gel, activated alumina, or bauxite, or refrigeration.

Carbon dioxide may be liquefied at any temperature between those at its triple point (-70°F) and its critical point (87.8°F) by compressing it to the corresponding liquefaction pressure. Two conditions are employed in commercial practice, the first near the critical temperature, with water being employed for cooling, and the second at temperatures in the neighborhood of 0°F to 20°F, with ammonia or other refrigerants being utilized for cooling. In the first method, liquefaction of the carbon dioxide is accomplished by compressing and cooling the gas until it is slightly below the critical temperature of 87.8°F at a pressure of 73 atmospheres or more. Low-temperature liquefaction of carbon dioxide is usually employed in cases in which the liquid carbon dioxide is to be used for the production of dry ice.

Dry ice. Solid carbon dioxide, popularly known as "dry ice", accounts for the greatest percent of carbon dioxide produced. In most of the larger installations in this country, solidification takes place directly in a hydraulic press where the blocks of dry ice 20 x 20 x 10 inches are formed. The blocks are subsequently cut up into 10 inch cubes weighing approximately 50 pounds each. In one method of dry ice press operation, carbon dioxide snowing takes place at the triple point and thus the evaporated gases are available for recycle at elevated pressures. After the snowing operation is

completed, the press chamber is vented down to atmospheric pressure thus releasing more carbon dioxide gas for recycle at low pressure.

The bulk of the carbon dioxide produced in this country is in the form of dry ice, most of which is used for preserving food by refrigeration. The advantages of carbon dioxide over water ice may be summarized as follows: (1) higher heat of fusion per pound, (2) lower storage temperatures are possible, (3) no residual water or brine results from melting. Other uses for solid carbon dioxide are more or less specialties and do not account for a large percentage of its production. They are: shrink fitting of machine parts, chilling of aluminum rivets before use in aircraft manufacture, chilling golf ball centers before winding, laboratory uses for cooling baths and sample freezing; refrigeration of serum and blood banks in hospital uses; "seeding" of clouds to precipitate rainfall.

Since carbon dioxide is shipped either as the solid or as the liquid in pressure cylinders, it is hard to separate the use for the liquid from the gas since either form may be obtained from the shipped material. Liquid carbon dioxide has been used as a refrigerant in mechanical refrigeration equipment, however, due to its relative inefficiency it is generally only used in applications requiring complete safety to operating personnel in case of leakage. It is used in considerable quantities in mining operations using the Cardox method of controlled vaporization blasting. Miscellaneous uses include: operation of bell buoys and railroad signals by the power produced from the expanding gas, inflating life rafts and many others.

The largest user of gaseous carbon dioxide is the carbonated beverage industry. Considerable quantities are also used in fire fighting equipment. It is used by the chemical industry as an inert gas blanket over reaction and storage vessels to prevent oxidation. Other chemical uses are mentioned in the section on reactions above. Miscellaneous uses include: air displacement in drying electrical cables, hardening concrete specialty products, scale removal from water pipes, as a respiratory stimulant, testing gas masks and humane killing of animals.

N. C. UPDEGRAFF

Physiological Aspects

Carbon dioxide, which is a by-product of the metabolic activity of all cells, is one of the most important chemical regulators in the human body. It can be truly said that human life without carbon dioxide would be impossible. In less specialized forms of life carbon dioxide is something to be gotten rid of; it is a waste product. In the more highly evolved animals, such as man, nature has used the gas to regulate the activity of the heart, the blood vessels, and the respiratory system.

Normal air contains about 0.03% by volume of CO_2 . A poorly ventilated room may contain as much as 1%. Concentrations of the gas from about 0.1 to 1% by volume induce languor and headaches; 8 to 10% concentrations bring about death by asphyxiation. High concentrations of the gas are toxic.

Resting men who are transferred from breathing room air to a mixture of 4.1% by volume of CO_2 in room air show an increase in expiratory minute volume from an average of 8 to about 15 liters; the respiratory rate increases from 14 to about 18 per minute; and the tidal volume from 0.500 to almost 0.900 liters. If the amount of carbon dioxide is increased, much greater increases (percentage-wise) in the above physiological measurements follow: expiratory minute volume, 420; tidal volume, 260; respiratory rate, 160.

As a general rule, the respiration of individual cells decreases as the concentration of carbon dioxide in the medium increases. Fish show a lessened capacity to extract oxygen from their environment with increasing amounts of carbon dioxide present. On the other hand, many invertebrates show marked increases in respiratory rate (or ventilation) with increased amounts of the gas in their surroundings.

Photosynthetic and autotrophic bacteria reduce carbon dioxide which is assimilated into complex molecules for use in synthesizing various cellular constituents. The gas is apparently assimilated, at least to a small extent, by the heterotrophic bacteria. Certainly it is required for any growth in these forms. Many pathogenic bacteria require increased carbon dioxide tension for growth immediately after they are isolated from the body. The production of hemolysins and like substances is greatly enhanced by adding 10 to 20% of CO_2 in the air which comes in contact with the cultures.

In men the average amount of CO_2 in the alveolar air is about 5.5% by volume; during the breathing cycle this concentration varies only slightly. In women and children somewhat lower mean values obtain.

The oxygen dissociation curve for blood is shifted to the right when the partial pressure of carbon dioxide in air is increased. This is referred to as the "Bohr Effect". It means that for a given partial pressure of oxygen, hemoglobin holds less oxygen at high concentration of carbon dioxide than at a lower. It is evident, then, that the production of carbon dioxide by actively metabolizing tissues favors the release of oxygen from the blood to the cells where it is urgently needed. Moreover, at the alveolar surfaces in the lungs the blood is losing carbon dioxide rapidly, which loss favors the combination of oxygen with hemoglobin.

In every 100 ml of arterial blood there is a total of 48 ml of free and combined CO_2 . In venous blood of resting man there is about 5 ml more than this. Only about $\frac{1}{20}$ of the carbon dioxide is uncombined, a fact which indicates that there is a specialized mechanism, aside from simple solution, for the transport of CO_2 in the blood.

About 20% of the CO_2 in the blood is carried in combination with hemoglobin as *carbamino-hemoglobin*. The balance of the combined carbon dioxide is carried as bicarbonate. A CO_2 dissociation curve for blood can be prepared just as for oxygen, but the shape is not the same as for the latter. As the partial pressure of CO_2 in the air increases, the amount in the blood increases; the increase is practically linear in the higher ranges. Oxygen

exerts a negative effect on the amount of CO_2 which can be taken up by the blood.

In working muscles large amounts of CO_2 are produced. It causes local vasodilation. The diffusion of some of it into the blood stream slightly raises the concentration there. It circulates through the body and the capillaries of the vasoconstrictor center, where it excites the cells of the center, resulting in an increase of constrictor discharges. If one recalls the stimulating effect of CO_2 on cardiac output, it is evident that a most effective mechanism exists for increasing circulation through active muscles. More blood is pumped by the heart per minute and the arterial pressure is increased by the general vasoconstriction; blood is forced from the inactive regions, under increased pressure, through the widely dilated vessels of the active muscles.

Narcosis due to CO_2 is characterized as follows: mental disturbances which may range from confusion, mania, or drowsiness to deep coma; headache; sweating; muscle twitching; increased intracranial pressure; bounding pulse; low blood pressure; hypothermia; and sometimes papilloedema. The basic mechanism by which carbon dioxide induces narcosis is probably through interference with the intracellular enzyme systems, which are all extremely sensitive to pH changes.

CHARLES G. WILBER

Cross-references: *Air, Blood, Photosynthesis, Oxides, Noxious Gases*

CARBON, INDUSTRIAL

Industrial carbons can be considered broadly as all forms of carbon used for industrial purposes excluding, however, carbon used simply as a fuel. Under this broad definition carbon becomes the most important single product type in the inorganic and allied product field. In 1952 only eighteen inorganic chemicals were produced in the U. S. in quantities exceeding one million tons. Industrial carbon led this list at 73,000,000 tons, worth over 1.5 billion dollars.

Of minor volume tonnage-wise, a significant dollar volume (over \$46 million in 1951) of industrial carbons is consumed as diamond, ballas, bort, and carbonado, whose use in abrasives, cutting operations, and die-orifices is indispensable.

Naturally occurring graphite is used for a wide variety of applications. The principal ones are lubricating, refractories, marking instruments, electrical products, corrosion resistant paints, and carbonizing of steel. Crude graphite ore is usually processed by air and/or froth flotation to remove impurities. Final processing can include sizing and/or grinding depending on the applications for which it is to be used. The present market for graphite is about 27,000 tons per year (1952). Total value of this market is \$4 million.

Manufactured industrial carbons are usually primary products or byproducts of fuel processing. They are used, either as is or after calcining, for a variety of purposes.

INDUSTRIAL CARBON RAW MATERIALS FROM FUEL PROCESSING

Coal	carbon black
coke	petroleum coke
char	residual oils
tar	carbon black
heavy oils	petroleum coke
carbon black	acid sludge
pitch	acid sludge coke
pitch coke	Natural gas
calcined coal	carbon black
de-ashed coal	Wood
Crude oil	charcoal
petroleum coke	pitch
distillate oils	lignin liquors
	activated carbon

By far the greatest use of industrial carbon, as defined, is in the iron and steel industry, where nearly 71 million tons of beehive and slot-oven coke were consumed in 1953. The major portion of this coke is used in the reduction of iron ore in blast furnaces. Coke produced by slot-oven coking of bituminous coal is the principal source of this form of industrial carbon. High-strength, large lump size, low ash, low sulfur, low phosphorus, and good reactivity are the major requirements for coke used in the manufacturing of iron in the blast-furnace process.

Anthracite, calcined anthracite, coal coke, and petroleum coke from the destructive distillation of residual oils are all used, in combination with coal tar pitch, for refractory pot linings, furnace linings, carbon bricks, and the like in such industries as the electrofining of aluminum, magnesium, and for lining of equipment to withstand unusual corrosion conditions. In this latter application, carbon or graphite pipe is often used for handling such chemicals as hot aqueous HCl , HF , etc.

Low grade coal cokes and chars of noncoking coals are used somewhat interchangeably with calcined and green petroleum coke in electrothermal processes for producing elemental phosphorus, silicon carbide, and calcium carbide, and in the reduction of zinc ore to the metal. In addition, the aluminum industry consumes large quantities of high grade calcined petroleum coke in the form of electrodes in the electrolytic reduction of alumina to aluminum.

Specifications of coke for the production of silicon carbide are not stringent, but those for coke for producing calcium carbide are somewhat more exacting. Low moisture ($<1.5\%$), volatile ($<2.0\%$), and phosphorus ($0. <1\%$) are the most important. Ash content of coke for this use can run as high as 4%. Apparent density is limited to 0.84 maximum while lump size should be between $\frac{1}{8}$ inch and 1 inch. It is also desirable that the coke or char be reasonably strong. Coke consumed by this industry was about 430,000 tons in 1954 or about 0.6 tons per ton of calcium carbide produced.

Typical analysis of coke used by elemental phosphorus producers is: 6 to 8% volatile; 3 to 5% ash; $-1'' + \frac{1}{8}''$ lump size. Again, strength and apparent density are important considerations although no specifications are set on these quali-

ties. Coke consumed by this industry was approximately 270,000 tons in 1950 or about 1.2 tons of carbon per ton of phosphorus.

Zinc producers use foundry coke to reduce zinc oxide to metallic zinc in the retort process. About 450,000 tons of coke were used in 1952 to produce 550,000 tons of retort zinc.

Specifications for petroleum coke used by the aluminum industry are very stringent. Moisture and volatile content of calcined coke should be less than 1.0%. Ash should be less than 0.8%, while silicon, iron, calcium, nickel, vanadium, and titanium content of the coke are all specified at levels less than 0.05%. Sulfur content should be less than 2%; for calcined coke, a minimum specific gravity of 2.0 is specified. Actually, carbon is not the primary reducing agent in this application. However, due to the proximity of the carbon electrodes to the high temperature reaction zone, the carbon in the electrodes is oxidized in this process to the extent that coke consumed by the aluminum industry was 600,000 tons in 1952 or 0.5-0.6 pound per pound of aluminum. In 1955, coke consumption is expected to be more than one million tons.

Fabricated electrodes made primarily from calcined petroleum coke find use in the electric arc or electrothermal furnaces for producing phosphorus, sulfur, silicon carbide, calcium carbide, magnesium, steel alloys, and many others. Consumption of coke by these industries, excluding arc-light carbons, was about 120,000 tons in 1950.

Charcoal from the destructive distillation of hard and soft woods is characterized by high surface area. This property is the basis for many of its industrial uses. This can be either for difficult reactions involving carbon, where charcoal presents more surface to react than other forms of carbon, or in cases where high surface for adsorption of colors or catalysts is desired.

The carbon disulfide industry consumes an average of 60,000 tons of charcoal yearly (i.e., about 30% of total charcoal production), mainly of the hardwood type. Specifications for charcoal used in the carbon disulfide industry are: low ash (2-2.5%), volatile (16-18%), and moisture (<4%) content, good lump strength and high bulk density.

Activated carbons consume about 50,000 tons of carbon per year (See *Carbon, Activated*).

Approximately 800,000 tons of industrial carbon worth \$110 million are sold annually to the rubber, paint, ink, and plastics industries. Ninety percent of this volume of carbon goes into rubber (e.g., tires) where it acts as a reinforcing agent, increasing abrasion resistance, and in general improves the physical properties of the finished product. Major applications for these carbons are in tires, mechanical goods, shoe soles, and heels. (See *Carbon Black*).

In summary, industrial carbons are vital raw materials for any modern industrial economy. The discovery of large new uses for industrial carbons is not imminent, but present uses for industrial carbons are expanding, particularly in such industries as aluminum and phosphorus,

which have grown at an unusual rate in the last few years. The largest single volume increase in demand for industrial carbons will be in the steel industry, where each one percent increase in steel production will require nearly one million tons of additional carbon.

At the present time increased demand for industrial carbons will be related closely to the predicted increase in gross national production which is approximately 4% a year.

C. A. STOKES, R. N. SECORD AND HANNA FRIEDENSTEIN

Cross-references: Coal and Coke, Carbon (Activated), Calcination, Graphite

CARBON MONOXIDE

Chemical Aspects

Carbon monoxide, CO, is a colorless, toxic gas with a peculiarly faint odor. In 1776 Lussone prepared the gas by heating charcoal with zinc oxide. Twenty four years later Cruickshank established the composition of carbon monoxide. It is used extensively as a reducing agent, an intermediate for the syntheses of a variety of organic compounds and in mixtures with other gases as fuel.

When combustion of carbonaceous materials takes place in an insufficient supply of air, carbon monoxide is produced. It is present in some furnace gases, the exhaust gases from gasoline engines and some volcanic gases. Manufactured fuel gases contain carbon monoxide as a principal constituent.

Preparation. Carbon monoxide, being in one of the lower oxidation states of carbon, is usually prepared either by high temperature reduction or partial combustion processes. Some of the high-temperature reduction methods are reduction of (1) oxides of zinc, iron or manganese with charcoal, (2) barium carbonate with carbon, (3) calcium carbonate with zinc or carbon, (4) carbon dioxide with zinc, iron, carbon or methane, and (5) steam with coke or methane. Partial combustion of coal, coke or methane yields carbon monoxide.

Carbon monoxide is also prepared by the degradation of selected compounds. Sulfuric or fuming sulfuric acid decomposes carboxylic acids like formic, oxalic, pyruvic and other alpha-ketoacids, glycollic, lactic, malic, citric, and trimethyl acetic acids and other compounds like hydrogen cyanide, formamide and potassium ferrocyanide with formation of carbon monoxide. Methanol is decomposed to carbon monoxide and hydrogen when vaporized at elevated temperatures over catalysts containing copper oxide and chromium oxide, or zinc oxide and chromium oxide. Methyl formate may be decomposed by warming in the presence of sodium methoxide to form essentially pure carbon monoxide.

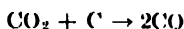
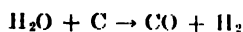
Commercial quantities of carbon monoxide are produced either by gasification of coal or coke or by partial oxidation of hydrocarbon gases. Perhaps the largest source is the gases produced from coal or coke by reaction with steam (water gas) and air (producer gas, blast furnace gas) or by heating (coke oven gas). All of these gases contain

varying proportions of components as indicated below.

COMPOSITIONS OF TYPICAL INDUSTRIAL GASES

Component	Blue Water Gas, % by Vol.	Producer Gas, % by Vol.	Blast-Furnace Gas, % by Vol.	Coke Oven Gas, % by Vol.
Carbon monoxide	37.8-42.8	22.0-26.0	26.2 27.5	5.0-6.8
Carbon dioxide	3.0-6.9	2.5-5.7	10.0 3.0	1.5-7.3
Hydrogen	49.2-51.8	3.0-13.2	3.0-3.5	47.3-57.0
Oxygen	0.1-0.5	0.0 0.5	0.1 1.0	0.2-0.6
Nitrogen	1.9-4.3	55.2-58.8	56.9 58.0	3.4-6.0
Methane	0.4-0.8	0.4-2.6	0.2-0.5	27.0 33.9
Illuminants		0.0-0.4		2.5-5.5

Water gas is most frequently used as a source of pure carbon monoxide or carbon monoxide-hydrogen mixtures. Higher proportions of carbon monoxide may be obtained by substitution of carbon dioxide for steam:



Purification. Several operations are required to obtain pure carbon monoxide from manufactured gases. Water scrubbing at atmospheric pressure or at 15 atm. removes suspended solids, ammonia, hydrogen cyanide, higher molecular weight sulfur compounds like thiophene, carbon dioxide and hydrogen sulfide. Scrubbing the gases with aqueous caustic or aqueous ethanolamine solutions removes acidic gases like carbon dioxide, hydrogen sulfide, carbon disulfide and carbonyl sulfide. Light oils and tars are removed from coke-oven gas by condensation, electrostatic precipitation and oil-scrubbing.

Liquefaction and absorption in aqueous solutions of cuprous salts are the methods usually employed for final purification of carbon monoxide. These methods are operable only with gases that contain no or insignificant quantities of inert gases like nitrogen. Water vapor and carbon dioxide must be removed prior to liquefaction, otherwise plugging of the equipment would result. Traces of nitric oxide must be avoided because it reacts to form explosive compounds at liquefaction temperatures.

The absorption method employs either an acid solution of cuprous chloride or an ammoniacal solution of cuprous carbonate or formate. Absorption is effected at ordinary temperature under a pressure of approximately 200 atmospheres. Carbon monoxide is recovered by releasing the pressure and heating the solution above 40°C. The gas may be purified further by a second cycle and is then scrubbed with water to remove hydrogen chloride or ammonia, and dried.

Detection. Methods employed for the detection of carbon monoxide are based either on its reducing property or its ability to form complexes. There are various methods available for quantitative estimation. In concentrations above 0.2 volume %, acetylene, ethylene, other unsaturates, and carbon dioxide are removed and

the carbon monoxide is absorbed in an aqueous solution of acidified cuprous chloride, an ammoniacal cuprous salt, or a commercial reagent known as "Co-sorbent", in an Orsat or Bureau of Mines apparatus.

Physical Properties. There are two solid forms of carbon monoxide with a transition temperature of -211.6°C , m.p. -200 to -205°C , b.p. -191.5°C , crit. temp. -138.7°C , crit. press. 34.6 atm., crit. density 0.311 gram/cc. The vapor pressures of the liquid in atmospheres at certain temperatures in $^\circ\text{C}$ are: 1, -191.5 ; 6.7, -170 ; 20.9, -150 ; 35, -139 .

The viscosity (10^6 poise) of gaseous carbon monoxide varies with the temperature ($^\circ\text{C}$) as follows: 56.1, -191.5 ; 127, -78.5 ; 166, 0; 172, $+15$; 210, $+100$.

The density of the gas at 0°C and 1 atmosphere is 1.250 grams/liter. For the liquid, d_4^{195} is 0.814.

Up to $T = 3000^\circ\text{K}$ the heat capacity of carbon monoxide in gram-cal./gram-mole at constant pressure may be calculated from the expression. $C_p = 6.055 + (2.4136 \times 10^{-3}T) - (5.478 \times 10^{-7}T^2)$. Similarly, the heat capacity at constant volume is given by the following expression where $t = ^\circ\text{C}$:

$$C_v = 4.970 + (1.7 \times 10^{-4}t) + (3.1 \times 10^{-7}t^2).$$

Its dielectric constant is 1.00070 at 0°C , and 1.00263 at -189°C . The thermal conductivity is 5.14×10^{-5} cal./sec./sq. cm./ $^\circ\text{C}$ /cm. at 0°C . The compressibility may be obtained by means of the van der Waals constants, $a = 2.96 \times 10^3$, and $b = 1.72 \times 10^{-2}$. Its dipole moment is low, 0.12.

Carbon monoxide is practically insoluble in water. At 0°C 100 g. of water dissolves 0.0044 grams, while at 100°C , 0.0000 gram. Its solubility is only several times greater in common organic solvents.

Thermodynamic properties determined by Clayton and Giaque are: heat of transition 151.3 ± 1 cal./gram-mole; entropy change on transition 2.457 cal./gram-mole/ $^\circ\text{K}$; heat of fusion 199.7 ± 0.2 cal./gram-mole; entropy change on fusion 2.933 cal./gram-mole/ $^\circ\text{K}$; heat of vaporization 1443.6 ± 1.0 cal./gram-mole; entropy change on vaporization 17.689 cal./gram-mole/ $^\circ\text{K}$; heat of formation from the elements $\Delta H^\circ_{298.1} = -26,620$ cal./gram-mole; free energy of formation from the elements $\Delta F^\circ_{298.1} = -33,000$ cal./gram-mole; standard entropy 47.316 cal./gram-mole/ $^\circ\text{K}$. Rossini gives for the heat of combustion $\Delta H_{298.1} = -67,623 \pm 30$ cal./gram-mole.

Chemical Properties. The inertness of carbon monoxide at ordinary temperatures and in the absence of catalysts or light is not surprising since its valence electronic structure is similar to that of the nitrogen molecule. At elevated temperatures, carbon monoxide is a potent reducing agent. Its availability at low cost, its reducing power and its versatility in catalytic addition reactions make carbon monoxide a valuable chemical in many commercial operations.

Stability. Carbon monoxide is stable with respect to decomposition into carbon and oxygen. However, it disproportionates into carbon dioxide and carbon at temperatures as low as 35°C over palladium deposited on silica gel. In the temperature range of 400 – 700°C almost any surface is

sufficiently active to give copious deposits of carbon. Above 800°C, the equilibrium favors formation of carbon monoxide.

Carbon monoxide burns with a bright blue flame to produce carbon dioxide. The reaction with oxygen is slow below 650°C in the absence of catalysts. At higher temperatures or when initiated with a spark, mixtures of carbon monoxide and oxygen containing trace quantities of water will explode. A catalyst containing oxides of copper and manganese, known as "hopcalite", has been used in gas masks to oxidize carbon monoxide to the harmless dioxide.

Carbon monoxide reacts reversibly with steam to produce carbon dioxide and hydrogen. The equilibrium constant of this reaction, the so-called water gas reaction, $K_p = (P_{CO} \times P_{H_2O}) / (P_{CO_2} \times P_{H_2})$, varies with temperature, °C, in the following manner: 226.0°C, 0.008; 426.9, 0.112; 626.9; 0.450; 1126.9, 2.17; 1526.9, 3.63.

Reduction of metal oxides. At temperatures from 300–1500°C, carbon monoxide reduces many metal oxides to lower metal oxides, metals or metal carbides. Among the metals whose oxides are so reduced are cobalt, copper, iron, lead, manganese, molybdenum, nickel, silver and tin. An interesting synthesis of $AlCl_3$ comprises reaction of CO and Cl_2 with Al_2O_3 in the presence of alkali. Carbon monoxide is the active agent, along with finely divided carbon formed by disproportionation, for the reduction of iron ore in the blast furnace. At temperatures above 900°C iron carbide, Fe_3C , is formed by the reaction of CO with Fe_2O_3 .

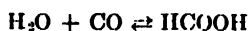
Metal carbonyls. The alkali and alkaline earth metals as well as certain of the heavy metals combine with carbon monoxide. The former appear to give salts, some of which are explosive, and the latter give true carbonyls. (See **Carbonyl Compounds**)

Miscellaneous inorganic reactions. Chlorine and bromine react with carbon monoxide under the influence of light or charcoal catalyst to produce phosgene, $COCl_2$, and carbonyl bromide. No reaction occurs with iodine, but carbonyl fluoride has been prepared by the action of AgF_2 on CO. The phosgene synthesis is highly exothermic, and is therefore favored by temperatures below 350°C.

Carbon monoxide reacts slowly with liquid sulfur and rapidly with the vapor to form carbonyl sulfide, COS.

Aqueous bases absorb carbon monoxide at ordinary and elevated temperatures with formation of formate salts. Sodium, potassium and ammonium formates are produced in this manner. The reaction is rapid at 200°C and high pressures.

Formic acid may be synthesized by addition of carbon monoxide to water:



The reaction is catalyzed by strong acids (HCl , H_2SO_4 , H_3PO_4) at 150–250°C, but for production of reasonably high concentrations of formic acid pressures from 1,000 to 3,000 atm. are required.

Reactions with organometallic compounds. Rather complex reactions occur with Grignard reagents

and carbon monoxide. Acyloins, alpha-diketones and olefins have been isolated. Ethylmagnesium halide with carbon monoxide gives butene-2 in yields up to 70% of theory. alpha Diketones and acyloins are formed from Grignard reagents derived from tertiary halides. Ketene is formed from iodomethylmagnesium iodide and carbon monoxide. Sodium alkyls react with carbon monoxide yielding ketones, tertiary alcohols and other compounds. See **Organometallic Compounds**.

Reactions of carbon monoxide and hydrogen. Products resulting from hydrogenation of carbon monoxide vary widely depending on catalysts and conditions employed. An almost infinite variety of organic compounds, including methane, benzene, paraffins, olefins, paraffin waxes, hydrocarbon high polymers, methanol, high alcohols, ethylene glycol, glycerol and other oxygenated compounds may be obtained.

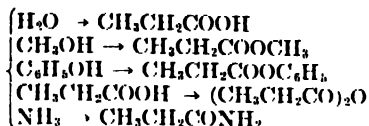
Reactions of carbon monoxide and alcohols. Depending upon the catalyst and conditions employed, carbon monoxide adds to alcohols to produce either formate esters or carboxylic acids and their esters. In the presence of alkali alkoxides, formate esters are produced. The reactions are reversible, and the direction taken is a function of the pressure at temperatures in the range of 50–250°C. When acidic catalysts are employed, the carbon monoxide is introduced into the alcohol between the O and C atoms resulting in the production of carboxylic acids and esters.

Reactions with organic halides. Hydrogen fluoride with boron fluoride as well as nickel carbonyl are effective catalysts for the addition of carbon monoxide to organic halides. When water is employed along with hydrogen fluoride and boron fluoride, carboxylic acids are produced. Acid fluorides are obtained in yields of approximately 80% when secondary chlorides or bromides are processed with carbon monoxide at –28 to 18°C and 600 atm. pressure in the presence of anhydrous hydrogen fluoride and boron fluoride.

Addition to dienes. Substituted 1,3 butadienes undergo the Diels-Alder reaction with carbon monoxide at high temperatures and pressures. 3-Methyl 3-cyclopentenone is the product from isoprene and 3,4-dimethyl 3-cyclopentenone, from 2,3-dimethyl-1,3 butadiene.

Reactions with hydrogen and olefinic compounds. In recent years the discovery that aldehydes and alcohols can be prepared in high yields from olefins, carbon monoxide and hydrogen, opened an interesting field of organic synthesis. This synthesis method is of importance in that it provides easy access to certain compounds and is of great practical value in industry. (See **Oxo Process**)

In the presence of either acidic catalysts or certain metal carbonyls, olefinic compounds, carbon monoxide and compounds containing active hydrogen atoms such as water, alcohols, phenols, carboxylic acids and ammonia or amines react to give carboxylic acids, esters, aryl esters, carboxylic acid anhydrides, and amides, respectively.



Boron fluoride, phosphoric acid and nickel carbonyl appear to be the most effective catalysts.

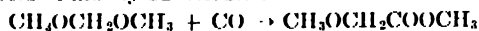
Reactions with acetylenic compounds. In 1939, Reppe, at the I. G. Farbenindustrie in Germany, discovered that compounds containing active hydrogen and carbon monoxide can be added to acetylenic compounds to produce acrylic acid and derivatives.



In addition to acetylene, substituted acetylenes, diacetylenes, alkynols, and acetylenes containing ether, ester, amine or mercaptan groups are operable. Other compounds containing active hydrogen atoms such as alcohols, thiols, carboxylic acids and ammonia or amines yield esters, thioesters, anhydrides and amides of acrylic acid or derivatives, respectively. (See **Acetylene**)

Miscellaneous organic reactions. Aliphatic ethers with carbon monoxide or carbon monoxide and water can be brought into reaction to give esters or acids. With dimethyl ether in the presence of boron fluoride and water at 200–300°C and 700 atm. pressure acetic acid and methyl acetate are formed. Of particular interest is the synthesis of adipic acid from tetrahydrofuran, carbon monoxide and water. The reaction is carried out at about 200°C and 200 atm. pressure in the presence of NiH_2 and Ni(CO)_4 using platinum lined equipment. Copper and silver lined equipment convert the iodine to inactive iodides.

Formals react with carbon monoxide in the presence of boron fluoride or other strong acids at 20–50°C. and 500–700 atm. pressure to produce esters of alkoxy-substituted esters.

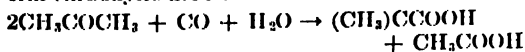


At 125–300°C. and 800–2,000 atm. pressure with cobalt catalysts, formals react with carbon monoxide and hydrogen to give alkoxy-aldehydes, with excess alcohol higher alkoxy acetals

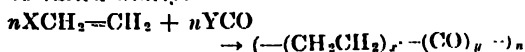
When aqueous formaldehyde is brought into contact with carbon monoxide at 125–225°C and 800–900 atm., and a strong acid (HCl , H_2SO_4 , or H_3PO_4) glycolic acid is produced. This synthesis is used commercially:



Ketones under comparable conditions yield several carboxylic acids.



Copolymers of ethylene and carbon monoxide are prepared at high pressures and temperatures with the use of free radical initiators. The ratio of ethylene to carbon monoxide in the polymer can be varied widely.



At 200–300 atm. and about 180°C carbon monoxide and hydrogen react with alcohols in the pres-

ence of cobalt carbonyl to produce higher homologs. From methanol chiefly ethanol, some *n*-propyl and *n* butyl alcohols are formed. When the pressure is raised to 3,000 atm., propylene glycol and its ethers are the chief products along with the higher homolog of the alcohol.

Uses. It is difficult to estimate the quantity of carbon monoxide consumed in industry. Undoubtedly the largest quantity is utilized as mixtures with hydrogen and other gases for industrial and domestic heating, and for the reduction of ores. An interesting example of its application is the Mond process for the recovery of nickel from ores containing iron, cobalt and copper. After the ore is concentrated and reduced with water gas at 300°C, it is treated with 80% CO at 50–100°C which converts nickel to its volatile carbonyl, Ni(CO)_4 . The vapor is removed and decomposed on metallic nickel pellets at 180°C as metallic nickel.

Smaller but substantial quantities of carbon monoxide are used in the manufacture of a variety of chemicals, such as olefins, waxes, methanol and higher alcohol, formic acid, acetic acid, glycollic acid, propionic acid, acrylic acid and esters, methyl formate, and butyraldehydes, from which innumerable derivatives may be produced.

Metal carbonyls, especially iron carbonyl, are manufactured for conversion by thermal decomposition to metal powders of high purity, which can be molded into complex articles by powder metallurgical techniques.

There continue to be extensive explorations of the reactions of carbon monoxide with organic compounds. Undoubtedly, this presages more extensive industrial applications of carbon monoxide in the future.

WILLIAM F. GRESHAM

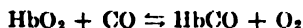
Physiological Aspects

Carbon monoxide is toxic to warm-blooded animals. Because of its extremely faint odor and taste, its lethal capacity can be insidious. The ordinary charcoal-filled gas mask is useless for filtering out carbon monoxide from contaminated air. Persons who are required to enter areas contaminated with carbon monoxide (firemen, rescue workers, maintenance men) must be provided with closed circuit breathing apparatus which delivers oxygen through a mask to the wearer. This is essential in atmospheres which contain more than 2% by volume of carbon monoxide. In atmospheres which contain less, an ordinary gas mask can be used for short periods, if it is fitted with a special canister filled with hopealite, a mixture of metallic oxides which serve to catalyze the oxidation of carbon monoxide to carbon dioxide. The reaction is exothermic and such canisters become very hot in use.

Carbon monoxide is physiologically quite inert, except for its strong combination with hemoglobin in the blood. It has no unique toxic action on any of the bodily tissues. As Henderson and Haggard point out: "Were it not for this one reaction carbon monoxide would be classified with nitrogen and hydrogen as a simple asphyxiant". The affinity of carbon monoxide for hemoglobin is about 300 times that of oxygen.

The reaction between carbon monoxide and

hemoglobin is reversible:



"Carbon monoxide displaces oxygen from hemoglobin, and in turn oxygen may displace carbon monoxide from its combination. Red corpuscles, in which the hemoglobin has been joined to carbon monoxide and then freed from the combination by means of oxygen, are not injured; they are capable of transporting oxygen as if they never had been exposed to the other gas. But so long as the combination with carbon monoxide continues they are incapable of fulfilling their respiratory function." Consequently, they cannot transport adequate oxygen to the various bodily tissues. Progressively severe anoxia results. Unfortunately, the victim is all too often unaware of his danger. Mechanical efficiency, e.g. driving a car, may persist until poisoning has advanced almost to the possibility of unconsciousness.

Death from inhalation of carbon monoxide can be summarized as follows: (1) reduction of the oxygen-carrying capacity of the blood due to the formation of HbCO; (2) tissue anoxia, especially in the brain, which is very sensitive to lack of oxygen; (3) consequent depression of respiratory center in the brain and decrease in respiration; (4) failure of the heart due to inadequate oxygen supply.

Carbon monoxide is absorbed into the body only through the alveoli in the lungs. It does not enter thru the eyes, mucous membranes, cuts, or upper respiratory tract.

Tolerance Limits. On the basis of numerous experimental studies, the tolerance limits for the average man have been established. The following series of equations gives a ready method for estimating the safety of any carbon monoxide-air mixture under conditions of rest. Time is given in hours and concentration of carbon monoxide in parts per 10,000 of air:

- a. Time \times concentration = 3 (no perceptible effect).
- b. Time \times concentration = 6 (a just perceptible effect).
- c. Time \times concentration = 9 (headache and nausea).
- d. Time \times concentration = 15 (dangerous).

Muscular activity or increased respiratory minute volume reduces the value in equation a to 1, 2, or less; it influences the other equations in like manner.

Drinker gives data on which the following table of allowable concentrations for carbon monoxide in air is based:

Concentration of Carbon Monoxide in		Effect
Per cent	Parts per 10,000	
0.01	1	No symptoms for 2 hours
0.04	4	No symptoms for 1 hour
0.06-0.07	6-7	Headache and unpleasant symptoms in 1 hour
0.1-0.12	10-12	Dangerous for 1 hour
0.35	35	Fatal in less than 1 hour

As a safe rule, based on sound experiments and experience, concentrations of carbon monoxide above 0.01 percent, or 1 part per 10,000, should not be permitted in houses, garages, laboratories, or industrial plants where prolonged exposure to the gas may be experienced.

Chronic Effects. There is no such physiological entity as "chronic carbon monoxide poisoning". The gas is not a cumulative poison; it is readily removed from the blood when the victim is exposed to pure air or oxygen.

After a severely acute exposure, the victim usually dies in about 36 hours or he recovers completely after a few days. The alleged chronic damage to man from carbon monoxide poisoning stems from prolonged cerebral anoxia which was severe enough to cause permanent brain damage but not severe enough to kill; it is not caused by retention of carbon monoxide in the body.

Treatment. The treatment of carbon monoxide poisoning depends on removal of the victim from the contaminated atmosphere, administration of artificial respiration, and inhalation of pure oxygen by the patient. If a good mechanical respirator is available, it can be used to advantage. In the absence of such device, air can be pumped into the victim's lungs by the Nielsen method of resuscitation, which is an arm lift-back pressure procedure. It is now the accepted method for administering artificial respiration in the Army, Navy, and Air Force.

The use of oxygen is essential for effective treatment. From the purely academic point of view, it might be argued that the addition of 5 to 7% carbon dioxide to the oxygen will result in more efficient resuscitation. On the practical level, however, there is little to justify the use of carbon dioxide during resuscitation.

Drugs are of little use and may even be dangerous. Under no circumstances should a patient who is recovering consciousness after carbon monoxide poisoning be permitted to arise and walk about. He must be kept in a prone or supine position; every effort must be made to keep his oxygen requirements at a minimum.

CHARLES G. WILBER

Cross-references: *Acetylene, Carboxylic Acids, Olefin Compounds, Carbonyl Compounds, Noxious Gases*

CARBONYL COMPOUNDS

The compounds containing the divalent C=O group, or *carbonyl group*, if considered together solely on this basis, undoubtedly comprise the largest and most important single class of organic compounds. Not only is a very large number of such compounds known, but these include many diverse types of substances, such as the proteins and amino acids, sugars, many perfumes and flavoring materials, medicinals and antibiotics, plastics like "Bakelite", "Textolite", "Lucite", and "Vinylite", paint resins such as the alkyds and "Glyptals", fibers such as silk, wool, rayon, nylon, and "Dacron", and many solvents and chemicals of industrial importance.

The carbonyl group may be considered most simply as a product of the oxidation of a hydrocarbon unit, $-\text{CH}_2-$ or $-\text{CH}_3$, although for economic reasons the introduction of a carbonyl group into an organic molecule generally is accomplished through the oxidation of an alcohol

group $-\text{COH}$ rather than by the direct oxidation

of a hydrocarbon. This oxidation of alcohol groups to carbonyl groups may be accomplished directly with oxygen at elevated temperatures in the presence of catalysts, by chemical oxidizing agents such as the permanganates, or by bacterial processes as in the production of vinegars. A few processes involve the reduction of more highly oxidized carbon compounds to carbonyl compounds, as in the chlorophyll-catalyzed photochemical reaction of carbon dioxide and water in living plants to form sugars. It should be remembered, however, that many important carbonyl compounds contain other functional groups in addition to the carbonyl group, and that the syntheses of such compounds often will employ simpler carbonyl compounds as starting materials.

We may divide compounds containing the carbonyl group into a few very general classes, depending on the nature of the two groups attached to the carbon atom of the carbonyl group. In all except a few compounds, the carbonyl group is attached to at least one organic group (designated generally as R in the examples below). For convenience, we refer to a functional group comprising a carbonyl group attached to one organic group $[\text{R}(\text{C}=\text{O})-]$ as an *acyl* group, and to specific examples such as the *acetyl* group $[\text{CH}_3(\text{C}=\text{O})-]$, or the *benzoyl* group $[\text{C}_6\text{H}_5(\text{C}=\text{O})-]$.

In the *aldehydes*, at least one of the attached groups is a hydrogen atom, and the group $-\text{C}=\text{O}$ is known as the *aldehyde group*. In all aldehydes except formaldehyde, HCHO , the carbonyl group also is attached to an organic group, as in acetaldehyde, CH_3CHO , or benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$.

The *ketones* are compounds in which the carbonyl group is attached to two organic groups. These may be the same, as in acetone, $\text{CH}_3\text{COCCH}_3$, or different, as in acetophenone, $\text{C}_6\text{H}_5\text{COCCH}_3$. When present in a ketone, the carbonyl group is sometimes referred to as the *keto* group.

In more highly oxidized derivatives, the carbonyl group is attached not only to an organic group but also to oxygen, through which it may be linked to other groups. These include hydrogen as in the *organic acids* $[\text{R}(\text{C}=\text{O})-\text{OH}]$, acyl groups as in the *acid anhydrides* $[\text{R}(\text{C}=\text{O})-\text{O}-(\text{C}=\text{O})\text{R}]$, or to organic groups as in the *esters* $[\text{R}(\text{C}=\text{O})\text{OR}']$. In formic acid, HCOOH , and its derivatives, R is hydrogen rather than an organic group. Common examples of compounds of these types are acetic acid, CH_3COOH , benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, and ethyl acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$. The $-\text{COO}-$ group is known as the *carboxyl group*.

Other derivatives of the acyl group include the *acid* (or *acyl*) *halides*, such as acetyl chloride, CH_3COCl , and the *acid amides*, such as acetamide,

CH_3CONH_2 . A very important compound related to the amides is urea, $(\text{NH}_2)_2\text{CO}$.

It should be appreciated that organic compounds can contain more than one carbonyl group, and that such groups may differ in functionality. For example, the common compound *aspirin* is *acetylsalicylic acid*, which is at once both an acid and an ester. In *oxalic acid*, $(\text{COOH})_2$, both carbonyl groups have the same type of functionality.

The chemical behavior of the carbonyl group depends upon the nature of the groups attached to it. In some types of compounds the carbonyl group generally is an active participant in chemical reactions, as in the aldehydes and ketones, while in others such as the organic acids and their derivatives, its primary action is to modify the functionality of neighboring reactive groups.

In the aldehydes and ketones, the carbonyl group is characterized by its unsaturation, and it is able to add a variety of reagents. This sort of reactivity resembles that of the carbon-carbon double bond, or olefinic linkage, but is somewhat greater because of the polar nature of the oxygen atom. Owing to the presence of the hydrogen attached to the carbonyl carbon, the aldehydes are considerably more reactive in general than are the ketones.

The aldehydes are very readily oxidized to the corresponding acids, and are intermediates in the oxidation of alcohols to acids. A very sensitive test for the aldehyde group, and one which often is used to indicate the presence of sugars (some of which are aldehydes), is the oxidation reaction with cupric ion in Fehling's solution. Ketones are less reactive toward oxidation and require more vigorous reaction conditions; they do not react with Fehling's solution, for example. In the oxidation of a ketone, two or more different organic acids will be formed depending on the nature of the groups originally attached to the carbonyl group. The reduction of a ketone leads to a secondary alcohol (RCHOHR'), whereas the reduction of an aldehyde leads to a primary alcohol (RCH_2OH). The reduction of an organic acid leads first to an aldehyde, then to a primary alcohol.

Of very great importance are the polymerization and condensation reactions exhibited by the aldehydes and, to a lesser extent, the ketones. In condensations of the *aldol* type, there is a transfer of hydrogen between molecules, from the carbon adjacent to the carbonyl group on one molecule (or from the carbonyl group in formaldehyde) to the carbonyl group on an adjoining molecule of aldehyde, thus forming an alcohol group and a carbon-carbon bond between the two molecules. The new molecule thus formed is both an aldehyde and an alcohol; hence the name *aldol*. This process can be repeated to build up more complex molecules. It is believed that the synthesis of sugars in living plants occurs by the condensation of simpler units, such as formaldehyde, through processes of this sort. The sugars then are converted into more highly condensed products such as the starches and cellulose. The simpler sugars include both keto and aldo types. In different types of reaction, the condensation of aldehydes, and formaldehyde

in particular, with phenols, with urea or derivatives thereof, or with casein, occurs readily to form resinous materials that are widely used in the plastics industries. One of the oldest and most common of these is "Bakelite". In the presence of strong acids, aldehydes may condense to form cyclical polyethers; some of these, such as para-formaldehyde, paraldehyde, and metaldehyde, are well-known articles of commerce. A number of industrial products and important chemical intermediates are prepared by the rearrangement of ketones.

In many of the reactions of aldehydes and ketones, and to a lesser extent organic acids, the reactivity of hydrogen atoms on carbon atoms adjacent to the carbonyl group becomes important through a process known as *enolization*, in which a hydrogen transfers from the adjacent carbon atom to the oxygen of the carbonyl group, leaving a double bond between the two carbon atoms. In the *enol* form, the hydrogen is highly reactive and very readily replaced by a variety of reactants; a molecular rearrangement follows such substitution in many cases. Aldehydes and ketones which have no hydrogen atoms on carbon atoms adjacent to the carbonyl group must remain in the *keto* form; such compounds are considerably less reactive and do not exhibit many of the reactions ordinarily characteristic of aldehydes or ketones.

In the organic acids and their derivatives, the primary function of the carbonyl group is to modify the reactivity of other attached groups. Thus for example, the functional hydrogen atom in acetic acid, CH_3COOH , is moderately acidic owing to the presence of the adjacent carbonyl group, and exhibits a number of reactions characteristic of acids, such as ionization in water, and the formation of salts, whereas the functional hydrogen in ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$, is essentially neutral. Similarly, the acyl halides, RCOX , are very reactive compounds, being readily hydrolyzed by water to form organic acids and hydrogen halides, whereas most of the alkyl halides, RCH_2X , are practically inert to water under ordinary conditions.

One of the more important reactions of acids, and also of acid halides, is esterification. The reaction of an acid or acid halide with the hydrogen of an alcohol group results in the elimination of water or hydrogen halide and the formation of an ester, e.g. $\text{RCOOH} + \text{R}'\text{OH} \rightarrow \text{H}_2\text{O} + \text{RCOOR}'$. This sort of reaction is used on a large scale industrially for the preparation of polyester resins, and synthetic fibers such as Dacron, as well as for the preparation of a variety of chemical specialties and intermediates. It may be considered as very roughly analogous to the neutralization reaction of an acid with a base.

In the amino acids, which are of the greatest importance since they are the basic units in the structures of animal and plant proteins, the amine group $-\text{NH}_2$ is present in place of one of the hydrogen atoms on the carbon atom adjacent to the carbonyl group, e.g. glycine, or aminoacetic acid, $\text{NH}_2\text{CH}_2\text{COOH}$. Since the amino acids are amphoteric, i.e. both acids and bases, they can undergo an unusual variety of chemical reactions, the amine group and the carboxyl group acting either

separately or together. One of the basic linkages in the structure of proteins is the peptide, or amide, linkage $-\text{NHCO}-$, which joins amino acid groups together into large polymeric molecules. This linkage is closely related chemically to the acid amides.

DALLAS T. HURD

Metal Carbonyls

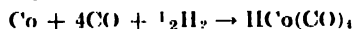
Carbonyls of heavy metals may be divided into two classes: those that contain only one metal atom in the molecule and those that contain two. Nickel carbonyl is known to be extremely toxic. Care should be exercised in handling all metal carbonyls. In the formation of metal carbonyls the electron pair of the carbon atom coordinates with the metal atom. Metal carbonyls are non-electrolytes like metallo-organic compounds. They are insoluble in water but are soluble in organic solvents such as benzene. Usually they can be distilled or sublimed. Carbon monoxide can be replaced from metal carbonyls by certain other electron donors ammonia, pyridine, phosphines, arsines, stibines, and isonitriles.

Usually two methods are employed for preparation of metal carbonyls. These are: (1) reaction of carbon monoxide with a finely divided, active metal at 50–200°C and 100–400 atm. pressure; (2) reaction of metal oxides, halides, sulfides or other salts with carbon monoxide in the presence of metallic copper or silver at elevated temperatures and pressures. Method (1) is applicable for the syntheses of nickel, iron, cobalt and ruthenium carbonyls. It appears that all the known metal carbonyls can be prepared by method (2).

All the metal carbonyls lose carbon monoxide when heated or exposed to light. Nickel carbonyl decomposes at about 43°C, and above, directly to the metal and carbon monoxide. Some of the others lose carbon monoxide in stages yielding carbonyls less rich in CO, less volatile, of lower solubility and of greater thermal stability.

Carbon monoxide exerts a poisoning effect upon nickel, copper, cobalt, and other hydrogenation catalysts and upon ammonia synthesis catalysts.

Metal carbonyl hydrides. Certain elements with an odd number of electrons combine directly with carbon monoxide and hydrogen to form metal carbonyl hydrides.



Rhodium, iridium and rhenium carbonyl hydrides are prepared in a similar manner. Iron carbonyl hydride is synthesized by treatment of iron pentacarbonyl with a strong base.

Cobalt carbonyl hydride, m.p. -26°C , decomposes at -18°C with evolution of hydrogen. Iron carbonyl hydride, m.p. -70°C , loses hydrogen at -20°C .

The metal carbonyl hydrides are acids. The ionic dissociation of iron carbonyl hydride resembles H_2S while that of cobalt carbonyl hydride, HCl . Various salts of the metal carbonyl hydrides are known.

WILLIAM F. GRESHAM

Cross-references: Carbides, Carbon Monoxide, Aldehydes, Ketones, Photosynthesis, Amines, Amides

CARBOXYLIC ACIDS

Carboxylic acids are those organic compounds

which contain the carboxyl group, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$. These compounds are acidic by virtue of the ionization of the carboxyl hydrogen. Although carboxylic acids are relatively weak in acid strength, their acidity is enhanced by the presence in the molecule of other carboxyl groups or negative substituents close to the carboxyl group, particularly in the alpha position in aliphatics, and the ortho position in aromatics.

Many carboxylic acids are found in nature, as free acids or in the form of esters or salts. Most natural aliphatic monocarboxylic acids are straight-chain acids containing an even number of carbon atoms. Those of higher molecular weight usually occur in the form of esters, in fats, oils and waxes. Among the most abundant are the saturated acids, palmitic and stearic, and the unsaturated acid, oleic. Some dicarboxylic acids, including oxalic, succinic, and fumaric, also occur in nature, as do the hydroxy acids, glycolic, lactic, ricinoleic, malic, tartaric and citric.

A limited number of aromatic acids are found in natural substances, notably benzoic and the hydroxybenzoic acids, salicylic, protocatechuic and gallic; and cinnamic and the hydroxycinnamic acids, *p* coumaric and caffeic.

Some natural alicyclic acids are abietic, chaulmoogric, hydnocarpic, and the bile acids.

There are several general methods for synthesizing carboxylic acids: (1) oxidation of a primary alcohol; (2) Grignard synthesis; (3) nitrile synthesis; (4) malonic ester synthesis; the monoalkyl malonic esters can also be used to prepare branched chain acids; (5) acetoacetic ester synthesis.

These methods are generally applicable to the preparation of aliphatic acids. Formic acid, however, is prepared by the addition of alkali to carbon monoxide at high temperature and pressure, followed by acidification of the resulting salt. Acetic acid can be made by the oxidation of acetaldehyde prepared from either acetylene or ethyl alcohol; and it can be isolated from the products of the destructive distillation of wood. Dilute acetic acid (vinegar) is made by fermentation of fruit juices to form alcohol, followed by bacterial oxidation. A number of high-molecular weight fatty acids are obtained commercially by hydrolysis of their naturally occurring glycerides. An acid hydrolysis is employed, in contrast to the caustic hydrolysis which is the basis of soap-making.

The higher dicarboxylic acids are generally prepared commercially by oxidizing certain alicyclic and aliphatic compounds. The acids having an even number of carbon atoms are more readily prepared by this method. Oxalic acid can be made by heating sodium formate, and also by fermentation. Catalytic oxidation of benzene yields maleic anhydride, which can be converted to succinic acid.

Alpha-hydroxy acids are conveniently prepared from the corresponding halogen compounds.

Esters of beta-hydroxy acids are produced by the Reformatsky reaction. The hydroxy acids which can be made by fermentation include lactic, citric and gluconic. Tartaric acid is obtained from potassium acid tartrate, a by-product of wine-making.

Some aromatic acids can be made by oxidizing aromatic hydrocarbons (e.g. benzoic from toluene, phthalic from naphthalene) or substituted acetophenones. Benzoic acid is prepared by the decarboxylation of phthalic acid and phthalic anhydride. Salicylic acid is made by the Kolbe synthesis.

Straight-chain aliphatic monocarboxylic acids containing fewer carbon atoms than capric are liquids, water-miscible up to butyric and thereafter decreasingly water-soluble. The acids beginning with capric are solids almost insoluble in water. All are quite soluble in most organic solvents. The acids containing an odd number of carbon atoms have lower melting points than the 'even acids' immediately preceding them in the series; boiling points increase regularly with increasing molecular weight.

Aliphatic polycarboxylic acids are crystalline solids, those of low molecular weight being relatively water-soluble. Dicarboxylic acids containing an odd number of carbon atoms have lower melting points and higher water solubilities than the 'even acids' immediately preceding them in the series. Alicyclic and aromatic acids are generally crystalline solids of low water solubility.

The following reactions are typical of carboxylic acids: (1) reaction with bases to form salts (RCOOM); (2) reduction to aldehydes (RCHO) and alcohols (RCH_2OH); (3) formation of acid anhydrides (RCOOCOR) and acyl halides (RCOX); (4) reaction with alcohols to form esters (RCOOR'); (5) amide formation ($\text{RCONR}'\text{R}''$); amides can be formed by heating ammonium or amine salts of the acid, or by reaction of an acid anhydride, acyl chloride or ester with ammonia or a primary or secondary amine; (6) decarboxylation to the hydrocarbon (RH), often achieved by fusing a salt of the acid with an alkali; (7) formation of ketones (R_2CO) by dry distillation of metal salts.

Formic acid undergoes several unique reactions. It is easily oxidized to water and carbon dioxide; heated with sulfuric acid it decomposes to water and carbon monoxide.

Aliphatic acids can be chlorinated and brominated in the alpha position in the presence of sunlight or an added catalyst.

Halogenated aliphatic acids react in different ways with alkali: α -halo acids are converted to α -hydroxy acids; β -halo acids form α,β unsaturated acids with elimination of hydrogen halide; γ -halo acids form lactones (intramolecular esters).

Aliphatic hydroxy acids are dehydrated on heating: α -hydroxy acids undergo bimolecular dehydration to give lactides; β -hydroxy acids form α,β -unsaturated acids; γ - and δ -hydroxy acids form lactones; where the hydroxyl group is removed by 5 or more carbon atoms from the carboxyl group, intermolecular esters or polyesters may be formed.

Dehydration of polycarboxylic acids leads to the formation of cyclic anhydrides where a 5- or

6-membered ring is possible. Higher molecular weight dicarboxylic acids yield polymeric anhydrides on dehydration. Dry distillation of some salts of dicarboxylic acids (adipic and higher) yields cyclic ketones.

The reaction of dicarboxylic acids with glycols forms polyesters, and with diamines, polyamides.

Oxalic and malonic acids undergo certain unique reactions. Oxalic acid on heating decomposes to carbon monoxide, carbon dioxide, formic acid and water; oxidation of oxalic acid gives carbon dioxide and water. Malonic acid on heating decarboxylates to form acetic acid and carbon dioxide; on dehydration it yields carbon suboxide. Maleic anhydride and other α,β -unsaturated anhydrides and acids undergo the Diels-Alder reaction with 1,3-dienes.

A few uses of some important carboxylic acids are listed below.

Formic acid is used in textile treatment and as an acid reducing agent.

Acetic and *propionic* acids are used in the production of cellulose plastics and esters. Calcium propionate is used as a mold inhibitor in foods.

Stearic acid finds application in rubber compounding as a dispersing agent and activator of accelerators. *Stearic* and *palmitic* acids and derivatives are used in the manufacture of soaps, candles, cosmetics, pharmaceuticals and protective coatings.

Oleic acid is employed in the manufacture of soaps and detergents, and in textile applications. Derivatives of *oleic*, *linoleic* and *linolenic* acids are constituents of paints and drying oils.

Acrylic, *methacrylic*, *maleic*, *fumaric* and *itaconic* acid derivatives are used in the preparation of a wide variety of polymers.

Oxalic acid is useful in rust removal, cleaning and bleaching. Other dicarboxylic acids, notably *phthalic*, *adipic* and *sebacic*, are employed in the preparation of plasticizers, alkyd resins, polyesters and polyamides. *Succinic* acid derivatives are used in a number of medicinals.

Citric and *tartaric* acids are used in foods, pharmaceuticals, and metal cleaners. *Citric*, *tartaric* and *gluconic* acids are sequestering agents. *Citric* esters find application as plasticizers in food wrappings.

Salicylic and *benzoic* acids and their sodium salts are antiseptics and preservatives. Acetylsalicylic acid (aspirin) and sodium salicylate are analgesics and antipyretics. Methyl salicylate is used in pharmaceuticals, flavors and toilet goods. Benzyl benzoate is an insect repellent and miticide.

Abietic and related acids are the chief constituents of rosin, used in the manufacture of paper, resins and varnishes.

Naphthenic acid salts, derived from crude oils, are used in paint driers, greases and soaps.

Some important carboxylic acids for which production data were listed by the U. S. Tariff Commission for 1953 are given in the following table.

Acid	Production, million lb.
formic (90%)	16
acetic	498
propionic	10
oxalic	19
chloroacetic	38
phthalic (anhydride)	227
salicylic	8
acetylsalicylic	14
2,4-dichlorophenoxyacetic	26

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Cross-references: *Acids, Aliphatic Compounds, Aromatic Compounds*

CARCINOGENIC SUBSTANCES

What are the factors which cause the transformation of normal tissues into cancerous growths? This transformation can be induced in all tissues which have the potentiality to proliferate, but it takes place with unequal readiness in different types of tissues in the same species and in the analogous tissues of different species. The principal factors to be considered as potential causes of cancer are: (a) The constitutional factors of the tissues of individuals and species, which are largely genetic in nature. There is, in addition, a substance which in certain strains of mice is transmitted with the milk from the mother to the offspring and which helps to determine the readiness with which mammary cancer and perhaps one other type of cancer develop in these mice; this substance is likewise hereditarily transmitted in various strains of mice. (b) Stimulating factors originating either within the organism itself or in the outer environment, which act on the cells and make them cancerous. The distinction between these two sets of factors, however, while very useful as an approximation, is not as sharply defined as it might appear, inasmuch as some hereditarily transmitted factors may function as growth stimuli, and conversely, stimulating factors may also be, at least partly, genetically determined. The character of the various stimulating factors may differ greatly in specificity. Among the most specific ones are (1) certain viruses, (2) hormones, and (3) certain metazoic parasites; next in order come (4) tar and the so-called carcinogenic (carcerigenic) hydrocarbons, which seem to be able to act on many tissues endowed with growth potentialities, and are specific mainly because of the great intensity with which they act. The least specific factors are those which not only may affect many tissues indiscriminately, but which act also with a lesser intensity, and are well known for other effects they may exert. To this group belong various radiations, as well as ordinary chemical and mechanical irritations, usually acting over long periods of time. The hereditary genetic factors function largely by determining the degree of responsiveness of a certain tissue to the various stimuli affecting it; but in some instances they may act indirectly by inducing certain diseases,

which themselves predispose to the development of cancer.

We shall now discuss the action of certain agents which produce cancer by chemical means. Of greatest importance are the carcinogenic polycyclohydrocarbons.

In 1914, two Japanese investigators, Yamagiwa and Ishikawa, discovered that if the ears of rabbits are painted with tar over long periods of time, at first warts, papillomas or cutaneous horns develop, and in the end true cancer of the epidermis may be produced. There seem to be, between the papillomatous stage and the stage of irreversible cancerous growth, intermediate stages in which, in the beginning, the stimulated epidermal cells invade in an abnormal manner the underlying tissues, but in which a spontaneous regression of these invasive processes sets in after cessation of the tarring. They interpreted these observations as an experimental proof that long-continued irritation may eventuate in the production of cancer. Subsequently, Tsutsui showed that the skin of the mouse responds much more readily to the painting with tar than that of rabbits.

It was found later that the active substances present in tar which were capable of inducing cancer under these conditions were contained in the fraction which passed into the distillate at a high temperature. These investigations suggested the search for pure substances contained in the tar which might be responsible for this effect. Kennaway *et al.* discovered a group of cancer-producing hydrocarbons which were derivatives of anthracene and phenanthrene. Later, Fieser, Shear, and others extended these investigations. The most effective ones among these substances are, in decreasing order of their effectiveness: 9:10 dimethyl-, as well as 5, 9, 10 trimethyl- 1,2-benzanthracene, 20-methylcholanthrene, 3:4-benzpyrene, and 1:2:5:6-dibenzanthracene. These substances induce cancer when they are painted on the skin of mice or injected subcutaneously at regular intervals over long periods of time, or when they are introduced in various places into the organism in the form of pellets. They cause a cancerous transformation in the organs and in tissues on which they act. The degree of potency varies with different preparations; slight alterations, such as the introduction of radicals CH_3 , OH , or of the cyano groups, may cause great changes in the intensity of the action of these compounds; also, the position of these radicals is of importance. Usually, the introduction of oxy-radicals diminished the effectiveness of such substances and the 5, 6, 9, 10 position in the anthracene ring seems to be especially favorable for the production of active preparations. Thus the Kennaways found that among five dimethylanthraces, the 9,10-compound alone produced epithelioma of the skin, and adenocarcinomas of the lungs. These tumors were most frequent in mice treated with this substance, but none of these preparations produced sarcoma after subcutaneous injection. However, there is no general rule concerning the factors determining the potency of these compounds which would apply to all, and which would

make it possible to predict whether a given compound will or will not be active.

Effect of Cigarette Tars. As stated above, tar was first used by two Japanese investigators to produce carcinoma of the ear in rabbits. Similarly other pathologists, such as Peyton Rous, have induced cancer in animals by painting their skin with this substance. We have also referred to the fact that the active cancer-producing agent in tar is probably the potent carcinogenic hydrocarbon, 3,4-benzpyrene.

In recent years it has been considered probable that the appearance of carcinoma of the lung in human beings is caused in a large proportion of cases by the smoking of tobacco, especially of cigarettes, which contain a tar-like substance. Actually, carcinoma of the lung is more frequently observed in men than in women, but with the increasing habit of the latter to smoke, it may be predicted that this type of cancer will also become more frequent in women in time. The delay in appearance of lung cancer is due to the long period of induction (latency) in the carcinogenic action of tar. The greater effectiveness of cigarette smoking as compared to cigar and pipe smoking in the induction of lung cancer may be attributed to the fact that it is customary with many smokers to inhale. It has also been suggested that the relative rise in temperature in the case of cigarette smoking, as compared to cigar and pipe smoking, may be partly responsible for this difference.

The conclusion that tobacco smoke is largely responsible for the increase in pulmonary carcinoma which has been noted in recent times found support in the experiments of Wynder and Graham and of others, who found that painting the skin of mice over certain periods of time with tar obtained from cigarette smoke caused cutaneous cancer. Quite recently Graham obtained a similar result in painting the skin of rabbits. In this species, however, the induction period is longer.

Other Compounds. We shall now mention some other compounds which have the ability to induce cancer by chemical processes. Perhaps the best known among these substances are the following: (1) *urethane* (ethyl carbamate), which acts as a mild anesthetic and induces tumors in the lung of mice, especially in those belonging to strain A, in which the occurrence of spontaneous lung tumors is very frequent, but also in some other strains. It may also induce tumors in the lungs of rats. Evidently it depends on genetic factors, which influence the responsiveness of the alveolar lung tissue. It is interesting that urethane, which has a definite carcinogenic effect in lung tissue, may inhibit the growth of various animal tumors and also the progress of leukemia, especially of the chronic myelocytic type, in man.

(2). In a similar manner the nitrogen mustards can induce pulmonary tumors, and inhibit other tumors. They show in certain respects a great similarity to the action of ionizing radiation; they are being considered as "radiomimetic" agents.

(3). In contrast to these two types of compounds in which the carcinogenic action is restricted largely to one organ, 2-acetyl amino-

fluorene is able to induce cancer in a number of different organs. Its action differs from that of the polycyclic carcinogenic hydrocarbons in that the latter induce cancer largely by contact action at the site of application; but they may also in certain instances act on distant organs. However, there is no radical difference between these two modes of action, inasmuch as also the distant action represents a contact action, brought about secondarily.

(4). Certain azo dyes, as for instance *o*-amino azotoluene and 1-dimethylaminoazobenzene, may after oral ingestion, induce carcinoma of the liver in rats and mice, but they are also able in some instances to induce cancer in various other organs, as for instance, in the urinary bladder. As usually a series of hypertrophic and hyperplastic growth processes precede the cancerous changes in the liver. Also application of chloroform and carbon tetrachloride may initiate similar types of tumors.

As to the carcinogenic action of inorganic substances, there are indications that arsenic preparations may induce cancer. There are various other inorganic substances, such as beryllium, cobalt, chromates, selenium, nickel and asbestos that may under certain conditions produce cancer. Cancer of bone, lung and skin in particular have been observed under special conditions. It seems that if a certain irritating, growth-promoting substance is deposited in close apposition to bone, it may here call forth first proliferation of bone-producing cells and ultimately sarcomas.

The substances mentioned so far are able to induce tumor formation, when tested experimentally in animals, or when man is exposed to their action occupationally or otherwise. There is one class of substance which may induce growth processes leading to the production of cancer as the result of their normal function. Such an effect is produced by certain hormones which induce growth processes in their end organs by chemical means. In 1915 and 1916 it was shown that ovarian hormones in collaboration with genetic factors were able to induce mammary carcinoma in mice. Ovariectomy performed at a sufficiently early age markedly reduced the cancer incidence in this organ. Likewise, prevention of breeding had a similar, although definitely weaker effect. At that time we suggested that some other hormones might exert a similar cancerogenic effect on their respective end organs; such actions have subsequently been established in the vagina, cervix, uterus, ovary and thyroid gland. Tumors may develop in the adrenal cortex after removal of the ovaries, which may exert an inhibition on the growth processes in the cortex.

In the case of the ovarian hormones we noted a proportionality between the length of time during which the hormone functioned and the number of resulting tumors. This cancer-producing action of hormones seems to depend on preceding growth processes which they induce, and such growth processes may be elicited by the hormones in cooperation with genetic factors, or in the case of the ovarian hormone estrogen, in cooperation with a virus-like substance. These cancerogenic hor-

mones (as well as carcinogenic hydrocarbons) may also exert an inhibiting effect on the growth of the tumors which they produced; but this antagonistic effect is weaker and more uncertain in its action than the tumor-inducing action. In the case of Roentgen rays the intensity of the radiation applied may determine whether they produce or destroy tumors; and urethane and nitrogen mustards may induce certain tumors and inhibit or destroy other kinds.

LEO LOEB

CARNEGIE INSTITUTION OF WASHINGTON

The Carnegie Institution of Washington was founded by Andrew Carnegie in 1902 under Articles of Incorporation that declared its purpose "to encourage in the broadest and most liberal manner investigation, research, and discovery, and the application of knowledge to the improvement of mankind." It is entirely independent of all other Carnegie agencies and the United States Government. The policy of the Institution is determined by a self-perpetuating Board of Trustees who meet in December of each year to consider the Institution's objectives and problems, to review its work, and to make appropriations for the following year. The policies of the Institution are administered by an Executive Committee chosen by and from the Board of Trustees, acting through the President of the Institution as chief executive officer. Andrew Carnegie originally endowed the Institution with ten million dollars, to which he added two million in 1907, and ten million dollars in 1911. At present, including special funds and an addition to the endowment from the Carnegie Corporation of New York, the resources of the Carnegie Institution of Washington amount to about fifty million dollars.

The research activities of the Institution are carried on through the seven departments listed below and a limited number of Research Associates, Visiting Investigators, and Fellows:

Mount Wilson Observatory, in California, is an outgrowth of the Solar Observatory founded in 1904. At present the Mount Wilson and Palomar Observatories are operated jointly by the Carnegie Institution of Washington and the California Institute of Technology, in a co-ordinated program of astronomical research on the structure of the universe and the nature and evolution of celestial bodies. Their joint equipment includes the 100-inch Hooker telescope on Mount Wilson and the 200 inch Hale telescope on Palomar Mountain, which has extended man's vision into space to over a billion light years.

The terrestrial sciences are represented by the Geophysical Laboratory and the Department of Terrestrial Magnetism, both located in Washington, D. C. The basic objective of the Geophysical Laboratory is to study the nature and composition of the earth and to learn as much as possible about the processes by which, during geologic ages, it has reached its present state. Much of the work of the Laboratory has dealt with phase equilibrium studies of silicate systems, which have afforded

exact information pertinent to rock formation. Other Laboratory studies have considered high pressure in its effect both on the properties of materials of the earth's crust and on the retention of dissolved water and other volatiles in solution in the molten magma. These and other studies of the Laboratory have a direct bearing on earthquake phenomena, mountain building, the nature of volcanoes and volcanic action, the genetic relationships of rocks and ore bodies, and the composition and physical state of the interior of the earth.

The Department of Terrestrial Magnetism was founded to conduct a broad program of surveys and studies relating to the magnetic and electric conditions of the earth and its atmosphere. After two decades devoted primarily to magnetic survey work, the major effort of the Department turned to basic problems in physics, including the ionosphere, cosmic rays, nuclear physics, radio astronomy, biochemistry, physics, and seismology.

Researches in the biological sciences are carried out through the Department of Plant Biology, the Department of Genetics, and the Department of Embryology. The Department of Plant Biology has its headquarters at Palo Alto, California. It devotes its attention to the means by which plants manufacture organic food and the evolutionary mechanisms by which they have reached their present great variation in form, size, and distribution. Much attention has been given to the nature of the plant pigments, chlorophyll, carotenoids, and phycobilins, and their part in the mechanism of photosynthesis. The Department also carries on active programs in experimental taxonomy and paleobotany.

The Department of Genetics, at Cold Spring Harbor, Long Island, New York, is primarily concerned with the biological mechanisms that determine the appearance of various traits and their transmission to succeeding generations. The Department studies such questions as the chemical composition and structure of the substances that transmit hereditary characteristics from parent to offspring, how they reproduce, the mechanism of their action in the cell and in the organ, and the factors which cause changes in structure and mechanism.

The Department of Embryology, at Baltimore, Maryland, is primarily concerned with the form and function of the human embryo. It conducts research in biophysics and in the physiology of the reproductive system, with special emphasis on pregnancy and embryonic growth. This Department has assembled the largest collection of human embryos in the world.

The Department of Archaeology, with headquarters in Cambridge, Massachusetts, has specialized in aboriginal American history, both in the United States and in the Mayan Area of southern Mexico and northern Central America. Extensive excavations have been made at Chichen Itza and Mayatan in Yucatan, at Uaxactun in northern Guatemala, and at Copan in Honduras. The collection and interpretation of Maya hieroglyphs is a specialty of the Department. Archaeological studies necessarily include studies in

ceramics, which have been greatly facilitated by the application of petrographic methods.

The present organization of the Carnegie Institution of Washington is the result of a continuing dynamic program. The pattern of organization has been flexible; units have been terminated as the work with which they were concerned was brought to completion or to a stage where conduct by other agencies was desirable; others have been linked or combined when such consolidation promised to be advantageous. Units terminated include the Department of Meridian Astrometry; the nonmagnetic sailing vessel *Carnegie*; the Department of Marine Biology at Tortugas, Florida; the Nutrition Laboratory in Boston; and the Desert Botanical Laboratory at Tucson, Arizona. Within the several departments organization and program are flexible and administered to enable the research worker to pursue the search for truth as he wishes, with full opportunity for discussion and co-operation with colleagues, and free from the distractions of teaching or administration.

Most of the research of the Carnegie Institution of Washington is published by individuals in current scientific journals. Interpretative reviews of work in progress are published in the annual "Year Book," and many of the completed studies are issued in a monograph series, which includes more than six hundred titles. These publications are distributed primarily to some five hundred libraries in scholarly and scientific centers throughout the world, which serve as the Institution's depositories. The Executive Offices of the Carnegie Institution of Washington are at 1530 P Street, Northwest, Washington 5, D. C.

GEORGE W. MOREY

CAROTENOIDS

Carotenoids constitute a unique class of natural coloring matters of widespread distribution in both plants and animals. They are elaborated in plants, and when ingested by animals, they may be absorbed, unchanged, or undergo modification. Definitions that attempt precision are apt to be arbitrary. The chromophoric system of carotenoids consists of a series of conjugated double bonds in a polyene chain in which an isoprene (methylbutadiene) pattern may be discerned. If the word "pigment" is included in the definition, compounds such as phytofluene, phytoene and vitamin A are automatically excluded, because six or seven double bonds in conjugation are required before the observer will perceive a pale yellow color. A further unique feature of the carotenoids lies in the mode of linkage of the isoprene units or residues. This may be explained best by reference to common carotenoids which have 40 carbon atoms in the molecule. Here, the two methyl groups closest to the center of the molecule are in positions 1:6 whereas the others occupy positions 1:5 relative to each other. (see Figure 1).

The C_{40} carotenoids may therefore be envisaged as comprised of two halves in each of which the isoprene pattern follows a head-to-tail sequence, with a tail-to-tail linking of the two halves. If the

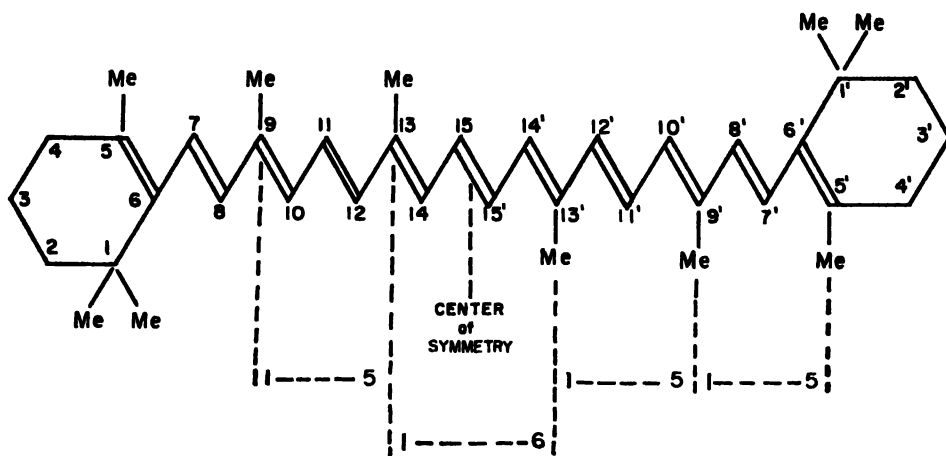


Fig. 1

end groups terminating the chain are identical, it is possible for the molecule to have a center of symmetry. Carotenoids with fewer than forty carbon atoms, of which several occur in nature, may be breakdown products (apocarotenoids) of C_{40} precursors. For the purposes of this definition, the "centers" of such molecules must be established by reference to a possibly hypothetical precursor.

Carotenoids are named after the principal pigment of the carrot root, carotene, $C_{40}H_{56}$, a mixture of two isomers, 5 to 10 per cent α -, and 90 to 95 per cent β -carotene. They may be classified as follows: (1) Hydrocarbons: (a) structural isomers of formula $C_{40}H_{56}$; (b) partially hydrogenated C_{40} compounds, particularly those forming a homologous series, $C_{40}H_{56}$, $C_{40}H_{54}$, $C_{40}H_{52}$, etc.; (c) synthetic carotenoids in which the C_{40} limitation imposed by nature has been surpassed. (2) Oxygenated derivatives: A wide variety of types is found: alcohols, esters, ketones, epoxides, furanoids, as well as combinations, e.g. alcohol, epoxide and furanoid. Acids and aldehydes are less commonly found and are the most likely to be true apocarotenoids, containing fewer than 40 carbon atoms.

The polyene chain with the isoprenic pattern is terminated by an ionylidene structure which may be related to α -, β -, or pseudoionones. d,l- ϵ -carotene, where the chain is terminated by two γ -groups, has been synthesized. The remainder are of natural occurrence, namely α -, p - and γ -carotenes and lycopene. Vitamin A, $C_{20}H_{30}O$, is one-half the β -carotene molecule, terminating at the C_{15} in a primary alcohol— CH_2OH . The relationship between vitamin A and carotenoids will not be further discussed except to remark that any carotenoid with one or more unsubstituted β -configurations is a potential vitamin A precursor.

The partially hydrogenated compounds are believed to be related to lycopene: neurosporene, from *Neurospora*, a tetrahydro-lycopene; ξ -carotene, pale yellow, an octahydro-lycopene; phytofluene, a green-fluorescing colorless compound; and phytoene. The series has attracted attention because of the suggestion that the common carot-

enoids arise by successive stepwise dehydrogenations. The hypothesis is by no means generally accepted at this time.

Interest in the synthetic carotenoids in which the C_{40} limitation has been surpassed lies chiefly in extending the range over which a relationship can be established between the number of double bonds in conjugation and the position of the spectral absorption maxima.

Oxygenated derivatives are found in all green leaves (xanthophylls), in many fruits, in egg yolks, crustaceans, and in many insects and fishes.

Carotenoids are a special class of polyene pigments. The presence of the methyl side chains necessarily modifies the breakdown products. Thus permanganate oxidation will yield some acetic as well as formic acid. Otherwise, the properties of carotenoids are those of polyenes in general. A deep blue coloration is yielded with concentrated sulfuric acid, also with As or $SbCl_5$ in $CHCl_3$, the Carr-Price reaction. The epoxy and furanoid derivatives also yield this color with concentrated HCl . The chromophore in a polyene chain arises from the possibility of charge separation. In the extreme case, with a ketonic oxygen ready to assume a negative charge, the presence of a proton acceptor or electron donor such as a protein would stabilize the form as effectively as the mineral acid. Thus in crustaceans, the carotenoid is linked with a protein and is usually green or blue in color. The carotenoid is liberated when the crustacean is plunged into hot water and assumes a red color.

Cis-trans isomerization. Most of the natural carotenoids are all-*trans* forms. However, *cis* isomers are possible. It was originally thought that the methyl group hindered and therefore restricted *trans-cis* rotations in the adjacent $-CH=CH-$ groups. While there appears to be some steric hindrance, studies with vitamin A indicate that "forbidden" rotations may in fact occur. The all-*trans* form has the lowest energy and possesses greatest stability. Isomerization occurs in the presence of heat, light, acid, and may also be catalyzed by iodine in the light. As a result of successive *trans-cis* rotations, there is progressive loss

in color. A *cis* peak, about 142 $m\mu$ from the position of the first band, at the longest wave length is to be noted. It is at a maximum for the central mono-*cis* compound, and is not discernible either in the all-*trans* or in the extreme poly-*cis* forms.

The majority of carotenoids crystallize readily. However phytofluene is a colorless oil, and ζ -carotene is not as yet well characterized as to crystal form.

The absorption spectrum of all *trans* carotenoids is typically 3-banded. The relationship between absorption maxima and number of conjugated double bonds may be deduced for carotenoids from work on the diphenylpolyenes. The carotenoids themselves do not form a homologous series, and the double bond in the β -ionylidene ring is equivalent to roughly one-half that in the chain.

Solubility and partition behavior. Carotenoids are soluble in the so-called "fat solvents". As the composition changes from hydrocarbon to the relatively highly oxygenated derivatives, solubility in more polar solvents (e.g. aqueous alcohol) becomes marked. Thus β -carotene and zeaxanthin can readily be separated by partition between petroleum ether and 80% ethanol. The first mentioned pigment is epiphasic (in the petroleum ether phase) while the latter is hypophasic. This applies only to the free zeaxanthin. Physalien, the ester, is epiphasic and must be saponified if it is to be separated in this manner from β -carotene.

Occurrence. Carotenoids are widely distributed in nature. Where they are the cause of pigmentation, they may occur up to 0.2% of the dry weight of the tissue involved. Where, as in blood plasma, β -carotene is usually to be found, the level is very much lower, and in this particular case, determined by the diet. While the sweet potato may have 0.1% or so of β carotene, the concentration in the white potato is rarely more than a few micrograms per gram. The latter is, in consequence, virtually devoid of color. Carotenoids in leaves are masked by the chlorophyll present.

G. MACKINNEY

Cross-references: *Pigments, Vitamins*

CAROTHERS, WALLACE HUME (1896-1937)

Wallace Hume Carothers was born in Burlington, Iowa, on April 27, 1896. His contributions to organic chemistry were recognized as outstanding and, in spite of the relatively short span of time for his productive accomplishments, he became a leader in his field with an enviable international reputation.

Leaving Tarkio College in 1920 with his bachelor of science degree, he enrolled in the chemistry department of the University of Illinois, where he completed the requirements for the master of arts degree in the summer of 1921. He returned to the University of Illinois in 1922 to complete his studies for the degree of doctor of philosophy, which he received in 1924. His major work was in organic chemistry with a thesis under the direction of Dr. Roger Adams, on the catalytic reduction of aldehydes with platinum-oxide platinum-black and on the effect of promoters and poisons

on this catalyst in the reduction of various organic compounds. He remained on the staff of the chemistry department of the University of Illinois as an instructor in organic chemistry from 1924-26 and then served in a similar capacity at Harvard University from 1926-28.

In 1928 the du Pont Company had completed plans to embark on a new program of fundamental research at their central laboratory, the Experimental Station at Wilmington, Delaware. Carothers was selected to head the research in organic chemistry, and he served until his untimely death in 1937.

In 1929 he was elected Associate Editor of the *Journal of the American Chemical Society*; in 1930 he became an editor of *Organic Syntheses*. His achievements were recognized by his election to the National Academy of Sciences in 1936—the first organic chemist associated with industry to be elected to that organization.

His early scientific work involved an extension to organic compounds of Langmuir's idea of isosterism. He demonstrated that it was valid in the case of phenyl isocyanate and azoimide. Reactions of the double bond were interpreted in terms of the electronic theory, using a point of view that has since gained wide acceptance.

His next efforts were devoted to demonstrating that any idea of "negativity" alone is inherently incapable of accounting for the relative reactivity of organic halides. He measured the base strength of a series of amines. His work on the thermal decomposition of alkali alkyls threw light on the inherent properties of the simplest organic anions.

The first field of which he was in a position to make an exhaustive study was that of acetylene polymers and their derivatives. With vinylacetylene and divinylacetylene made available to him, he completed a detailed study of these substances. It was his discovery that it was possible to add hydrogen chloride to monovinylacetylene with formation of 2-chloro-1,3-butadiene, called chloroprene. This substance is analogous structurally to isoprene but polymerizes several hundreds of times more rapidly and leads to a product much superior to all previously known synthetic rubbers. It was the first synthetic material to show rubber's curious property of developing fibrous orientation when stretched and instantly reverting to the amorphous condition when released from stress. In resistance to aliphatic hydrocarbons and to most chemical reagents it is definitely superior to natural rubber. It has, moreover, a greater resistance than rubber to corona and sunlight. Carothers' work laid the foundation for the development by other chemists and by chemical engineers of the du Pont Company of the commercial product which has found wide industrial use and which is marketed as neoprene.

These initial ideas culminated in the publication of a series of thirty-one papers in the field of polymerization. In these he proposed a general theory of condensation-polymerization and a logical and systematic terminology suitable for use in this previously disorganized field. The implications of his theory were illustrated by a series of experimental studies dealing with polyesters, hy-

drocarbons, polyamides, and polyanhydrides. These studies provided experimental material for correlating chemical structure and physical properties of materials of high molecular weight, and furnished evidence of favoring a view now generally accepted for the structure of such natural high polymers as cellulose. In these investigations a new technic—molecular distillation—was applied to the propagation of chemical reactions.

In this study a method new in principle was developed for the synthesis of many-membered cyclic compounds. A large number of many-membered cyclic compounds was synthesized, including several of entirely new types. Some of these compounds had musk-like odors and are otherwise similar in their properties to the genuine musks. One of these new many-membered ring compounds has found industrial application. The large amount of experimental material made possible important deductions bearing on the relationship between chemical structure and ease of ring formation. His contribution was a major one to the field of many-membered ring compounds, which is one of growing significance in organic chemistry.

He investigated the means by which polymers structurally analogous to cellulose and silk could be prepared, and synthesized a large number. These materials constituted the first completely synthetic fibers with a degree of strength, orientation, and pliability comparable with natural fibers. Their study made possible the development of a theory for the relation between structure, fibrous properties, and other physical properties. The work was brilliant and the most important aid in recent years to the understanding of such polymers. This information, and the modification of the physical and chemical properties of polymers by slight changes in the mode of preparation made possible the exploration of a wide variety of substances of most promising industrial application, culminating in the synthesis of nylon. These contributions are recognized by the naming of the du Pont polymer research laboratory as the Wallace Hume Carothers Laboratory.

(Abridged from memoir for National Academy of Sciences.)

ROGER ADAMS

Cross-references: *Fibers (Synthetic), Polymerization*

CASEIN

Casein is the principal protein in milk and the chief ingredient of cheese. Caseins derived from the milk of different mammals are similar if not identical in composition and properties. The usual source is cow's milk, which contains 3% of casein. Skim-milk left after separation of cream from whole milk owes its white, turbid appearance to colloidal dispersed particles of calcium caseinate and calcium phosphate. There are 3×10^{11} particles in a cubic centimeter, ranging from 8 to 200 mm in diameter. The enzyme rennin converts casein to paracasein and coagulates calcium para-

caseinate. Acids release casein from combination with calcium and dissolve calcium phosphate, whereupon free casein precipitates; the calcium salts remain in the whey.

Pure casein is an amorphous, tasteless, odorless, white solid. Commercial casein is slightly yellow with a pleasant odor. When dry and protected from insects and rodents it keeps well but damp casein molds and becomes disagreeably odorous. Casein is hygroscopic; at 90 and 30% relative humidity it holds about 23 and 9% of moisture, respectively, based on the dry weight. The specific gravity when dry is 1.25 to 1.31.

Like other proteins, casein is a macromolecular substance composed of at least 15 amino acids that include, in decreasing order of content, glutamic acid, hydroxyglutamic acid, proline, valine, leucine, lysine, tyrosine, arginine, aspartic acid, phenylalanine, histidine, alanine, tryptophane, proline, and methionine. Casein belongs to the class of phosphoproteins; it contains 0.85% of organic phosphorus and 0.76% of organic sulfur. The amino acids are joined through the peptide linkage, $R-NH-CO-R'$, to form macromolecules or micelles of flexible, coiled spiral structure and effectively spherical overall shape. The micelles, even as they exist in milk, differ in size stepwise, in a range of "molecular weight" from 75,000 to 375,000, so that at least four fractions can be identified and separated, known as α -, β -, γ -, δ -casein. Casein, therefore, may be considered a mixture of four or more closely related proteins.

Casein is amphoteric and is isoelectric at pH 4.6, where its solubility in water is minimum at 0.01%. Below pH 4.6 acids form moderately soluble salts like casein chloride; above pH 4.6 bases form salts like sodium caseinate. Alkali salts are soluble in water without limit; alkaline-earth and heavy-metal salts are nearly insoluble. Casein is a lyophilic colloid akin to albumin and gelatin and serves readily as a protective colloid and as an emulsifying agent. Solutions of caseinates form gels when slowly coagulated from concentrated solution. Casein and its salts are insoluble in most organic solvents. Formaldehyde forms a very insoluble compound with casein. Paracasein, commonly called rennet casein, is somewhat less lyophilic but otherwise almost identical with casein.

Naturally soured casein is made from skim-milk, rarely from buttermilk, by keeping the milk at 90 to 110°F until it curdles. Five to 10% of sour whey from a previous lot may be added to speed the process. Fermentation of milk sugar (lactose) by ever-present bacterium *Streptococcus lactis* produces lactic acid to decalcify and precipitate the casein. To make acid casein, warm skim-milk is acidified with dilute HCl or, less often, H_2SO_4 in sufficient quantity to precipitate the casein. The acid process may be operated continuously. After precipitation the whey is drawn off, the curd washed thoroughly, drained or pressed, ground, and dried at a temperature not over 165°F. The HCl method permits recovery of lactose from the whey.

To make rennet casein, warm skim-milk is "set" with rennet extract at 104°F until calcium paracaseinate clots. The clot is cut into small pieces,

the whey drawn off, the curd washed, drained or pressed, ground, and dried. The product contains combined calcium and calcium phosphate. Decalcified rennet casein may be made by further treating the curd with acid.

The United States consume 50 to 75 million pounds of casein annually. From 1934 to 1942 domestic production exceeded 46 million pounds annually; from 1943 to 1951 it was less than half as much and since 1952 less than 8 million pounds annually. The balance is imported. About 70% of the consumption is for coating paper, 25% for making glues, paints, and plastics, and 5% for many diverse uses, among which are prepared foods, medicines, cosmetics, seasoning and dressing leather, cleaners and polishes for white shoes, textile printing and sizing, insecticide sprays, and soap making.

Industrial uses of casein depend chiefly on its colloid properties of gelation, film formation, emulsification, protective action, and good adhesion. Since other proteins and synthetic macromolecular substances have similar properties the position of casein is highly competitive. In no major use does casein enjoy clear-cut superiority over all alternative materials.

Paper coatings. Book and art papers are made smooth enough to receive half-tone illustrations well by coating them with pigmented casein. A water slurry of suitable pigments is incorporated in a mildly alkaline solution of naturally soured or acid casein. Formaldehyde or lime may be added to improve resistance to water. The mixture is applied in a coating machine and then dried.

Glues. Casein glues make strong joints that resist dampness for some time, though they are surpassed in water resistance by modern resin glues. Casein glues are used chiefly for woodworking and plywood, less often for joining wood, paper, or other moisture-permeable material to metal or glass. Naturally soured or acid casein is mixed dry with lime, one or more sodium salts whose corresponding calcium salts are nearly insoluble, and sometimes a fungicide. For use the dry mixture is stirred in water, whereupon the lime and sodium salts promptly dissolve and react to form sodium hydroxide, which dissolves the casein as sodium caseinate and makes a strongly alkaline solution, viscous enough for gluing. In further action an excess of lime converts sodium to calcium caseinate, which slowly coagulates, together with the insoluble calcium salts to a strong, irreversible gel.

Paints. Casein may be used (1) for the vehicle or binder of paint or (2) as an emulsifying agent in the more recent emulsion paints and latex paints, all of which are thinned with water. The first may be powder paint, similar in composition to casein glue except for the further addition of pigments, or it may be paste paint, in which the pigments are dispersed in a mildly alkaline solution of naturally soured or acid casein, to be diluted with water to brushing consistency for use. In the second casein serves the necessary but subordinate purpose of preventing coalescence of emulsified droplets of oil-, varnish-, or resin-

vehicle and perhaps also of preventing agglomeration of dispersed pigments.

Plastics. Casein plastics resemble horn, ivory, and marble. The chief use is for buttons for clothing. Rennet casein is granulated, moistened and softened with water, kneaded, and dyes or pigments added for color. The mixture is extruded in rods or tubes from a heated screw-press. The soft plastic may then be molded in the desired shape after which it is hardened by long soaking in formaldehyde solution and finally dried slowly.

Textile fibers that resemble wool can be made by extruding an alkaline solution of casein through spinnerets, strengthening the fibers by stretching, and hardening them in an acid bath containing formaldehyde. The fibers may then be woven, felted, or used as bristles.

FREDERICK L. BROWNE

Cross-references: *Proteins, Textile Chemistry, Colloid Chemistry, Adhesives*

CATALYSIS

For many years it has been recognized that certain substances by their very presence are able to alter the rate of chemical reactions. It was not until 1835, however, that this phenomenon was given a name. *Berzelius* called these substances "catalysts" and named the phenomenon "catalysis". The name appears to have been well chosen. It was derived from two Greek words: "kata", meaning *entirely* and "lyo" meaning *loose*. The implication of the name is to the effect that a catalyst loosens the bonds of the reactant substances in such a way as to greatly alter the rate of reaction. At the time, it was decided that catalysis was due to some special "catalytic force". It is now generally recognized, however, that the forces involved are probably those of ordinary chemical reactions. The exact mechanism by which catalysts operate is still not certain. There certainly would be no disagreement among chemists, however, that catalysts do in some way "loosen up" the bonds of reactants and profoundly alter reaction rates.

Strictly speaking, catalysts can either increase or decrease the rate of a reaction. A very large fraction of the literature on catalysis is devoted to systems in which the catalyst *increases* the rate. The retardation reactions, called negative catalysis, is known to exist, however. One common theory of the action of negative catalysts is that they combine with and remove from the system traces of positive catalysts, or that they combine with intermediates in a chain reaction in such a way as to break the reaction chain. In the remainder of this description the discussion will be limited to the action of catalysts in accelerating chemical processes.

It is frequently stated that a catalyst is a substance capable of altering the speed of a reaction without itself necessarily undergoing any chemical change. It must be recognized, however, that according to present points of view a typical catalyst as it operates in a reaction may well have been altered considerably from the form in which

it was added to the reactants. The changes are especially notable in the composition of the surface layer of a catalyst, though in many instances changes throughout the body of the catalyst may also take place. For example, if an iron catalyst is placed in contact with a mixture of hydrogen and nitrogen at 450°C, the iron immediately becomes covered with a chemisorbed layer of nitrogen, hydrogen and perhaps even ammonia molecules. Furthermore, the catalyst becomes saturated with dissolved nitrogen and dissolved hydrogen. It may even be true that these added gases influence the electronic characteristics of the solid catalysts in such a way as to be controlling factors in the activity of the iron as a catalyst.

A more extreme instance of a change in the catalyst during use is afforded by the iron catalysts that are active in the synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen. Such a catalyst, which initially consists mostly of iron, changes very rapidly to a mixture of carbides and Fe_3O_4 . A certain small amount of the original alpha-iron also usually persists. It is important to know, however, that during the various changes in the solid phase of the catalysts, the activity often continues at a fairly steady level. It might perhaps be more accurate to say that the solid which is initially added to a reaction and which is commonly called a catalyst undergoes rapid changes in the presence of reacting gases to some form in which the surface becomes a combination of metal, reactant, and product atoms or molecules, the exact composition of which is often unknown. The persistence of activity for long periods of time indicates, however, that this surface layer presumably reaches a steady state and does not change extensively, even though the underlying bulk phase, may become altered as a function of time.

Another important characteristic of a catalyst is the fact that a formula weight of catalyst will usually be effective in participating in the transformation of many formula weights of reactants. For example, iron synthetic ammonia catalysts are known to have operated effectively for periods of several years, in the course of which thousands or even millions of formula weights of ammonia per formula weight of catalyst were produced. Eventually, catalysts lose their activity due to gradual sintering, accumulation of poisons, the occurrence of side reactions between the catalyst and one or more of the reactants, or the accumulation of products. In practice they may have to be regenerated every few minutes or not for years, depending upon the reactants, the catalyst, and the operating conditions.

Catalysts merely speed reactants toward their normal chemical equilibrium but do not actually alter the position of equilibrium. Thus, for example, if a mixture of three parts hydrogen and one part nitrogen is placed in contact with an iron catalyst at 450°C and a total pressure of one atmosphere, the final equilibrium amount of ammonia will correspond to 0.23% of a gaseous phase. This figure therefore represents the upper limit of the per cent ammonia that can be produced in a stream of 3:1 hydrogen to nitrogen gas over an iron

catalyst at this particular temperature and at atmospheric pressure. It must be kept in mind that in complex reactions a catalyst frequently can yield many products. It does not always follow that the products formed will be those which would be obtained if equilibrium existed among all the various products. For example, cetane can be cracked over a silica-alumina catalyst to a variety of hydrocarbons. It is well known that the ratio of isobutane to normal butane obtained as a reaction product at a given temperature is always considerably in excess of the ratio that would exist if these gases were in contact with the catalyst long enough to permit sufficient isomerization of iso- to normal butane. It so happens in this instance that under operating conditions the cracking reaction occurs at a relatively faster rate than the isomerization reaction among the reaction products.

Catalysts may be solids, liquids or gases. If the reactants and catalysts comprise two separate phases, as in the case of gases reacting over solids, or liquids reacting in the presence of finely divided solids, the phenomenon is frequently referred to as *heterogeneous* catalysis. On the other hand if the catalyst and the reactants are all dispersed as a homogeneous phase, the process is usually designated as *homogeneous* catalysis. Iron catalysts for the synthesis of ammonia represent a good example of heterogeneous catalysts; on the other hand, acids in solution may act as catalysts for different components of a liquid phase by a process of homogeneous catalysis. Most of the present discussion is devoted to heterogeneous catalysis but a few brief remarks will also be made relative to some of the essentials of homogeneous catalysis.

Preparation and Nature of Solid Catalysts. Catalysts may consist of elements, compounds or amorphous mixtures of complexes or compounds. Among the elements, the metals are particularly useful as catalysts. Among compounds, metallic oxides and metallic sulfides are outstanding. Probably the principal example of an amorphous mixture of complexes or compounds is the silica-alumina catalyst used in cracking hydrocarbons.

One important characteristic of catalysts is that they are usually highly specific in their activities. For example, a catalyst may well be active for the hydrogenation of certain bonds of organic compounds and yet completely inactive for the hydrogenation of other bonds. Thus, iron catalysts produced by the reduction of the oxide have been shown to be capable of hydrogenating ethylene at temperatures as low as -100°C; for this reaction they have activities comparable with the activity of nickel catalysts. On the other hand, these same iron catalysts are incapable of hydrogenating benzene to cyclohexane even at 200°C, whereas nickel catalysts are very active for this reaction at room temperature. This property of a catalyst—to be specific in regard to its action—is extremely important. In those systems in which a multiplicity of activities might be involved, this specificity of catalysts is for the most part an inherent characteristic of a given surface. Moreover, it is also dependent to a certain extent upon the pore size and pore distribution of the catalyst.

For example, catalysts for partial oxidation should presumably have a pore size sufficiently large to lower the probability of oxidation of the desired intermediate product to carbon dioxide and water while it is passing out of the pore structure of the catalyst into the main gas stream.

Traditionally, catalysts are prepared in such a way as to produce large surface areas. They are therefore usually either finely divided or porous or both. For the maintenance of a large surface area of the catalytic component, use is frequently made of substances which in themselves are inert, but which are capable of supporting the active catalyst in a form that resists sintering. Common supports are alumina, kieselguhr, silica gel, and even silica-alumina catalysts.

Evidence very strongly suggests that the activity of a catalyst is often centered in only a small fraction of the catalyst surface. The nature of these active points or active regions is still very much a matter of dispute. Sometimes they are created by adding impurities known as *promoters*. For example, the addition of about 1% of potassium oxide and 1% of some inert oxide such as aluminum oxide to an iron oxide catalyst yields on reduction a porous iron solid partially covered with these added promoter materials. Such catalysts are much more active at high pressure than those produced by the reduction of pure iron oxide or those catalysts containing, for example, only aluminum oxide as promoter. It thus appears that one must attribute some intrinsic activity to the interface between the promoter components and the metal surface. Regardless of the nature of the active regions, there is no question but that the surface of most solid catalysts is very non-uniform in activity. The actual preparation of catalysts frequently involves the reduction of metallic oxides or compounds to the metal form after the addition of necessary promoters. The oxides themselves are prepared in an amorphous or finely crystalline condition by precipitation under proper conditions and in the presence of suitable promoters.

Catalysts are usually subject to poisoning. This involves the deposition of certain impurities in such a way as to render the active centers or active portion of the catalyst surface inactive. For example, traces of hydrogen sulfide in a stream of hydrogen will usually cause a rapid decrease in the activity of a metallic hydrogenation catalyst. These poisons may be temporary and capable of being removed by some suitable treatment of the catalyst for a short period of time by one or both of the pure reactants; or they may be incapable of being removed by such procedure and will become permanent. For example, traces of oxygen or water vapor in a hydrogen-nitrogen mixture will serve as temporary poisons for an iron catalyst. However, treatment of the catalyst at normal operating temperature by a stream of pure hydrogen or pure hydrogen and nitrogen will rapidly remove this oxygen poison and thus regenerate the catalyst. In contrast to this, during the cracking of hydrocarbons over silica-alumina catalysts, carbonaceous deposits are built up on the catalysts. These deposits have to be periodically removed

by combustion in order to restore the catalyst to its initial activity.

Exact details of the nature of the catalyst surface cannot at the present time be specified. A recent trend tends to classify catalysts as being metals, semiconductors or insulators. This classification throws emphasis on the electronic structure of the solid as a very important one in determining the nature and extent of catalytic action. It is also currently popular to interpret the "active points" or "active regions" of catalysts in terms of lattice defects that have been built up in a catalyst by the addition of impurities, by the removal of certain atoms from the original compounds to produce non-stoichiometric compounds frequently characterized by high conductivity, or by the preparation of the catalyst in such a way as to produce numerous lattice irregularities or dislocations. Much more experimental work will be required before the exact nature of the catalyst surface can be described with any certainty.

To illustrate the types of catalysts and types of reactions that are especially important, a limited number of examples are itemized in the accompanying table. Attention is also called to current commercial use that is being made of certain of the catalysts and reactions.

Type of Catalyst	Typical Catalysts	Reactions Catalyzed
Acid	silica-alumina	Cracking of hydrocarbons
	HF	Alkylation
	H ₂ SO ₄ , H ₃ PO ₄	Isomerization of hydrocarbons
Hydrogenation-dehydrogenation	H ₃ PO ₄	Polymerization of olefins
	Ni	Oils to fats
	Fe	Ammonia synthesis
	Fe, Co	Hydrocarbon synthesis
	Pt, Pd, Rh	Hydrogenation of double bonds and other carbon linkages
	Fe ₂ O ₃ , MoO ₃ , Cr ₂ O ₃	High temp. dehydrogenation
Cyclization and aromatization	ZnO, Cr ₂ O ₃	Methanol synthesis
	Pt, MoO ₃ , Cr ₂ O ₃	Heptane to toluene
		Straight-chain hydrocarbons to cyclic and aromatic hydrocarbons
Oxidation	V ₂ O ₅ , MoO ₃ , WO ₃	Partial oxidation of organic compounds
	Ag ₂ O	Ethylene to ethylene oxide
Hydration-dehydration	Fe ₂ O ₃ , Cu ₂ O-CuO,	Complete oxidation
	Pt, MnO ₂ , Bi ₂ O ₃	
	Al ₂ O ₃ , ThO ₂	
Halogenations	Metallic halides	Deacon process
Dual Type	Pt, MoO ₃ , or Cr ₂ O ₃ on acid type supports	Hydroreforming of hydrocarbons

Mechanism of Catalytic Reactions. From what has so far been stated, it is evident that the mechanism of catalytic reactions must be as obscure as the nature of the catalyst surface itself. Progress is being made in elucidating both the mechanism of the reactions and the nature of the catalyst surface. It seems to be generally agreed

that solid catalysts invariably combine chemically at the surface with one or more of the reactants. This combination is referred to as *chemical adsorption* or *chemisorption*. For example, both nitrogen and hydrogen are capable of being chemically adsorbed on iron catalyst at the temperature at which these gases are capable of combining to form ammonia. Silica-alumina cracking catalyst for cracking hydrocarbons in the temperature range of 400° to 500°C are sometimes cited as an exception to this rule. The most recent data, however, seem to indicate that chemical interaction between the reactants and this catalyst surface does actually occur, but takes place on only a very small fraction of the surface of the catalyst.

The action of the metallic catalyst has for many years been related to the geometric spacing and arrangement of the metal atoms with respect to the molecules of the reactants. Thus, for example, Beeck found that a plot of the spacing of the atoms of pure metal films against the activity of these films for the hydrogenation of ethylene yielded a curve with a maximum corresponding to activities larger by several orders of magnitude than the activity of some metals lower on the curve. Thus, a thin film of rhodium was, per unit area at a given temperature, about 1000 times as active as a thin film of nickel.

More recently, this difference in activity has been attributed to the electronic characteristics of the individual metals. Beeck showed that his data can be represented as a smooth curve if the logarithm of the activity per unit area of catalyst is plotted against the per cent *d*-character of the metal, as interpreted by the Pauling hybridized bond theory of metals. In a very spectacular demonstration of the way in which the electronic characteristics of a metal may influence activity, Dowden and Reynolds showed that adding copper to nickel gradually filled the "d-band vacancies" in the nickel and at the same time lowered the activity of the catalyst for the hydrogenation of styrene. As a matter of fact, the activity dropped to approximately zero when enough copper had been added to make the alloy consist of 40 atom per cent copper and 60 atom per cent nickel. This result was interpreted as indicating that one or both of the reactants on the catalyst surface tended to transfer electrons into the lattice of the solid. It must be pointed out, however, that for the hydrogenation of other molecules, catalysts containing certain amounts of copper are definitely more active per unit area than nickel itself. For example, the rate of hydrogenation of ethylene to ethane has been reported to be many-fold greater for catalysts containing 20 to 50 atom per cent copper than for pure nickel.

For oxide catalysts, such as vanadium pentoxide, molybdenum trioxide, zinc oxide, and chromium oxide, evidence is accumulating to indicate that the steady state composition of the solid which catalyzes a reaction is definitely different from that of the original stoichiometric compound. It is also known that the electrical conductivity of these compounds changes by many orders of magnitude as lattice defects are built up. These defects, in some instances, are produced by adding

excess oxygen (p-type semiconductors) and in some instances by removing atoms from the initial stoichiometric compound (n-type semiconductors). Although definitive data for correlating the conductivity of a semiconductor with its activity as a catalyst are for the most part still lacking, there seems to be little doubt that the creation of lattice defects is important in and perhaps essential to the catalytic action of solids. Some workers in the field believe that all catalytic reactions are controlled essentially by the electronic characteristics of the solids. Others admit that certain reactions are so controlled, but that some reactions, such as catalytic hydration and dehydration, may take place by mechanisms that are not concerned with the conductivity of the solids.

In conclusion, it may be well to mention a few of the newer research tools that are now available to help unravel the factors that are important in producing active catalysts. These include methods for measuring the surface area of a finely divided or porous catalyst (see **BET Theory**); for measuring the pore size and pore distribution of catalyst; and for obtaining values of the electrical properties of the catalyst particles. In addition, electron diffraction, x-ray diffraction, and the electron microscope are yielding valuable information about the solid phase and in some instances about the surface layer of the solid catalyst. Finally the use of radioactive and nonradioactive tracers is helping to elucidate the way in which certain catalytic reactions take place. For example, tracer experiments employing radioactive alcohols, aldehydes and other oxygen compounds seem to establish that the synthesis of hydrocarbons over metals such as iron takes place through formation of an oxygen complex on the surface by the interaction of carbon monoxide and hydrogen. These various tools and approaches should in the years immediately ahead furnish a very much better picture of the nature of catalyst surfaces and catalytic action than is available at present.

Homogeneous Catalysis. The action of a homogeneous catalyst is, in a sense, less complex than that of heterogeneous catalysts. For the most part catalysis in homogeneous systems seems necessarily to involve the formation of intermediate chemical complexes. For gaseous reactions catalyzed by gases this is usually particularly clear-cut. For example, nitrogen pentoxide is known to catalyze the decomposition of ozone. This catalysis apparently takes place as a result of nitrogen pentoxide decomposing into lower oxides of nitrogen plus oxygen. The lower oxides of nitrogen then react rapidly with ozone to produce oxygen and to regenerate nitrogen pentoxide. This process repeats itself, until all the ozone is exhausted. The rate of ozone decomposition under these circumstances will be governed by the intrinsic rate at which nitrogen pentoxide decomposes.

In homogeneous catalytic reactions occurring in solution, the interpretation of results is frequently much more difficult than for homogeneous gas catalysis. This is due to a number of factors. To begin with, catalysts and reactants in solution

are subjected to all the numerous variables that characterize reactions in liquid phase. These include phenomena of ionization in solution, complex formation, salting out effects, activity coefficients of reactants and catalytic components, and specific effects to be associated with the solvent medium and the presence of various added substances, which in some way affect the properties of the solutions.

Probably most examples of homogeneous catalysis fall in one of two classes. These may be designated as acid-base catalysis and oxidation-reduction catalysis. In the former category are the many reactions in solution that apparently are catalyzed by protons or hydronium ions on the one hand, or by hydroxyl radicals on the other. In the second category are reactions such as the decomposition of hydrogen peroxide capable of being catalyzed by the various metallic ions, such as those of copper, nickel, cobalt and iron. In this connection, it should be pointed out that fantastically small amounts of copper ion have been shown to have positive effects on certain reactions. Concentrations as low as 10^{-13} molar for copper ions in solution will produce a definite catalytic effect on the catalytic oxidation of sulfite ion to sulfate. It should perhaps also be pointed out that for just such systems the action of negative catalysts is most pronounced. Any substance capable of combining with some of these minute traces of positive metal ion catalysts would cause enormous changes in the rate of reaction, even though the negative catalyst might be present in quantities comparable in magnitude to the traces of positive ion that are effective for the reaction.

Typical examples of homogeneous catalysis include the acid-catalyzed inversion of sucrose; the decomposition of hydrogen peroxide into water and oxygen as catalyzed by various metallic ions; the isomerization of *cis* and *trans* ethylenic compounds by iodine; and the oxidation of sulfite ions to sulfate ions by oxygen in the presence of various metallic ions.

In conclusion it should be mentioned that enzymes are naturally occurring organic catalysts. They are distinguished by the fact that they catalyze reactions that are essential to processes of human, animal, and plant metabolism. Some enzymes have such low molecular weights that they may be classed as homogeneous catalysts; others are part of such large molecules that they can probably best be classified as heterogeneous catalysts. They are characterized by an astonishing specificity and by a very high order of effectiveness (See *Enzymes*).

PAUL H. EMMETT

CATIONIC AGENTS

Cationic agents exhibiting surface activity are those compounds in which, on ionization, a positive charge resides in that portion of the molecule containing the long hydrocarbon moiety. Associated with this cation is a negatively charged ion, usually, though not necessarily, a halide, acetate, methosulfate or hydroxyl. Such a molecule is di-

rectly opposite in character to the anionic agents, the soaps, alkyl sulfates, alkyl aryl sulfonates, etc. However, because of the internal balance of hydrophobic and hydrophilic groupings, the cationics exhibit marked surface activity and are often referred to as "invert" soaps. Included in this classification are the arsonium, phosphonium, isothiuronium, hydrazonium, alkyl ammonium, quaternary ammonium, etc. salts, of which the latter two are the most important, chemically and economically.

The production of cationic surface-active agents has risen from 5 million pounds, valued at 3.66 million dollars, in 1945, to 58 million pounds, worth some 20 million dollars, in 1953. In general, the members of this group of compounds have common functions, centering about their high germicidal activity, their ability to act as emulsifiers and wetting agents, their detergent properties, and their substantivity, their tendency to plate out on negatively charged surfaces, imparting a hydrophobic, water-repellent surface film.

The cationics, except for the free amines, are generally salt like in character, water-soluble and hydrocarbon-insoluble. They are usually prepared and used in the form of the hydrochloride, the acetate or the fatty acid salt, although any compatible mineral or organic acid may be used. The amines are organic bases, water insoluble and hydrocarbon soluble, and, like the other members of this group, are incompatible with the anionics. A double decomposition type of reaction occurs, usually producing an insoluble product.

The cationics can be divided, roughly, into nitrogen- and non-nitrogen-containing compounds. The latter group includes the sulfonium, arsonium, antimonium, phosphonium, etc. salts. Of these only the phosphoniums have achieved any commercial significance, and only to the extent of 1-2% of total cationic sales in 1952. They are, at the moment of little commercial value, although they tend to parallel the quaternary ammonium salts in activity.

The nitrogen-containing cationics include the primary, secondary and tertiary amines and their water-soluble salts, and the quaternary ammonium salts derived from the amines.

Considering the amines first, they probably represent the bulk of the cationic materials produced in this country, although published figures do not always distinguish between these and the quaternary ammonium salts. The simplest of the amines are the mono- and di-alkyl-amines, or their salts, which ionize in water.

These surface-active primary, or symmetrical secondary, amines are prepared by the catalytic hydrogenation of the corresponding nitriles and are sold under the trade name "Armeens". Production of these compounds has been climbing rapidly, although they were unknown commercially before ca 1940.

The long-chain primary amines are distillable organic bases, irritating to the skin, and toxic. The symmetrical secondary amines are much higher boiling and much less toxic. Their salts behave as colloidal electrolytes in solution and tend to undergo micelle formation; they show

marked surface activity and are generally polymorphic. Chemically, the primary amines are extremely reactive, containing two active hydrogens on the nitrogen atom. They form carbamates on exposure to CO_2 in the air; thioureas and dithiocarbamates with carbon disulfide; double salts or complexes with inorganic metal salts; addition compounds with conjugated double bonds; salts and amides with fatty acids; isocyanates with phosgene; can be alkylated (with ethylene oxide or methyl chloride, e.g.), etc. The salts of the symmetrical dialkyl amines are especially interesting in that, though polar compounds, the large hydrocarbon moiety tends to make for solubility in hydrocarbon solvents.

The amines and their salts may be used as selective flotation agents, for the separation of KCl from NaCl, e.g. where introduced air bubbles float the hydrocarbon-coated particles; as asphalt additives, for the prevention of wet-weather stripping from the aggregate; as pigment grinding or dispersing agents; as corrosion inhibitors, by the deposition of films impervious to water, CO_2 , and O_2 ; as lubricating aids, etc. There are, in addition, a host of miscellaneous applications such as their use as internal mold-release agents, as extrusion lubricants and scorch retarders in butyl rubbers, as slow-drying caulking compound additives, as cutting oils, as color flushing agents, as anti-static agents, and as base compounds that can be fully alkylated to the corresponding quaternary ammonium salts.

The other large group of non-quaternary nitrogen-containing cationics is the amido-amines, prepared by reacting a fatty acid and a polyamine.

The amine reactant may contain more than two amino groupings and may also contain other functional groups, such as the hydroxyl, so that many representative samples of this class of compounds are possible. Many have been prepared commercially.

The imidazolines are another group in the nitrogen-containing cationic agent classification. These are prepared by the thermal cyclization of an amido-amine containing a free secondary amine function.

Among the other miscellaneous classifications that should be listed here are the ester amines (from the fatty acid and dimethyl ethanolamine or triethanolamine, e.g.); aniline derivatives, in which the nitrogen is attached directly to the aromatic ring (dodecyl aniline, e.g.); iso-thiouonium salts; glycine esters of long-chain alcohols; amine addition products to maleates; vinyl pyridines; cyclic nitrogen containing compounds; (pyridines, quinolines, benzimidazolines) guanidines; tertiary amine oxides; ether containing amines; oxazolines ("Alkaterge"); urethanes; morpholines; etc.

The other large subdivision of cationic agents is that comprising the quaternary ammonium salts. Quaternary ammonium salts are cationics containing a pentavalent nitrogen atom, of the general formula $(\text{R}_4\text{N})^+\text{X}^-$, where the $\text{R}'\text{s}$ are any alkyl, aryl or heterocyclic grouping, the same or different, and X is an anion, usually halide or methanesulfate.

The quaternary ammonium salts may be formed

from any of the cationics mentioned above which can be isolated as the free base. Quaternization occurs directly, with tertiary amines, by heating with an alkylating agent, e.g. methyl chloride, benzyl chloride, dimethyl sulfate, etc. With primary and secondary amines, alkali (sodium hydroxide or bicarbonate) must be present to neutralize the hydrochloric acid formed in the reaction and allow it to proceed to completion.

Although the quaternary ammonium salts were known from the early 1900's, they were essentially a laboratory curiosity until ca 1935, when interest in these salts was revived with the discovery of their highly bactericidal properties. Production of these compounds, in 1946, was about 1.1 million pounds, valued at \$930,000; in 1952, production rose to 4.2 million pounds, worth \$3.2 million, a high point in quaternary production. Expectations are good, however, that production will increase, and probably has already, beyond this level.

The quaternary ammonium salts ionize as true cationic salts, give very strongly basic quaternary ammonium ions on treatment with alkali and are soluble, generally, in water and insoluble in hydrocarbons. Those prepared from the symmetrical dialkyl amines, however, are hydrocarbon soluble too. Variation in anion and cation can be quite extensive, so that wide differences are possible in physical and chemical properties.

Quaternary ammonium salts, like the amine salts, are usually white crystalline solids or viscous liquids, quite hygroscopic, decompose on heating (to the corresponding tertiary amine, generally) form micelles at specific concentrations, are adsorbed on negatively charged surfaces and are generally incompatible with anionics and certain proteinaceous materials. The hydroxides of these salts cannot be isolated as such, but exist in solution as very strong bases. Analysis is well defined and accurate to several ppm., using indicator titration or colorimetric techniques, and the salts are usually non-toxic and non-irritating at most internal or external use concentrations (ca 1:1000), although wide variations are noted in individual compounds.

The largest number and variety of applications of the quaternary ammonium compounds center about the ability of these compounds to inhibit or kill organisms. From a bactericidal standpoint they are extremely efficient, with phenol coefficients in the 300-400 range. Killing efficiency increases with pH, and the optimum chain length centers about 16 carbon atoms, although varying functional groups and organisms will affect this optimum. Inactivation of hard water is more pronounced toward Gram (-) organisms, killing dilutions vary from 1:7000 to 1:60,000 depending upon organism and molecular configuration, and water solubility is generally good, making for general applicability as a disinfectant.

The quaternary ammonium salts have been used in the sterilization of dental and surgical instruments, as post-operative skin and wound sterilizers, in urological, obstetrical and gynecological applications, for sanitizing fruit before squeezing for frozen juice, in operating room clean-up and

scrub work, for creamery machinery and food-establishment utensil clean-up, for egg treating, as a preservative (anti-mold agent) in casein base paints and liquid starches, as an algae controller in swimming pools and cooling systems, as an anti-fungicide, etc.

Their ability to retain moisture and act as conductors, coupled with their tendency to be adsorbed on certain textiles and plastics, makes them promising anti-static agents. In addition, they serve as textile detergents and assistants and supply a soft "hand" to some fabrics and papers. They are especially good softeners for cotton fabrics.

The quaternary ammonium salts form acid stable emulsions and wetting agents (they have no detergent properties on the alkaline side), for herbicides and insecticides, for the fat liquoring of leather, for depositing mineral oil on metals (as anti-corrosion agents), etc.

They function as dye assistants, by reducing dye solubility and giving greater fabric deposition, as dye levelling agents and penetrants for cellulose fibers, and in improving the wash fastness of colors.

Pharmaceuticals containing quaternary ammonium groupings exhibit antispasmodic and parasympathomimetic activity.

In addition, the quaternary ammonium salts exhibit certain miscellaneous functions: they act as foam rubber latex sensitizers, as lubricants and corrosion inhibitors in cutting oils, as wetting agents in buffing sticks, as demulsifiers (by precipitating anionic foamers), as grease additives (by an interchange reaction with bentonites) and in secondary oil recovery work by destroying impeding organisms and sulfur producers (eliminating corrosive by-products) and acting as pore penetrants and oil releasers.

The cationics as a class do not approach the volume production of the anionics, of course, but their versatility and inherent properties make them a good potential bet for increased production and application.

M. R. MCCORMICK and PAUL DUBROW

Cross-references: *Amines, Soaps, Detergents*

CAVENDISH, HENRY (1731-1810)

Henry Cavendish, the English chemist and physicist, is remembered chiefly for his research on gases demonstrating the constitution of water and nitric acid. He was born on October 10, 1731 in Nice. As the nephew of the third duke of Devonshire, he was an extremely wealthy man. However, he lived a simple life using his money almost solely to support his avid interest in natural science. He was a shy, almost hermit-like individual but seldom missed a meeting of the Royal Society of which he was a fellow. He was not interested in fame or learned degrees and his formal education at Peterhouse, Cambridge was not completed. He never married and died in his home at Clapham on Feb. 21, 1810.

He was an ingenious and accurate experimenter but many of his papers remained unpublished until long after his death. He adhered to the phlogiston

theory, although he admitted that his findings could be explained with equal facility by the principles enunciated by Lavoisier.

In his work on gases, he developed methods for drying them with anhydrous potassium carbonate, storing them over mercury and correcting volumes for variations in temperature and pressure. He investigated the preparation and properties of hydrogen which he recognized as substantially pure phlogiston. By means of his metallic eudiometer, he clearly demonstrated the formation of water by the reaction of hydrogen with oxygen (dephlogisticated air). This technique also enabled him to synthesize nitric acid from the nitrogen of the air (phlogisticated air). In carrying out these experiments, he reported that approximately $\frac{1}{120}$ of this phlogisticated air could apparently not be converted to nitric acid. This evidence of the existence of the inert gases remained unexplained for approximately 100 years. These discoveries on the synthesis of water and nitric acid were published in two papers which appeared in the *Philosophic Transactions* in 1784 and 1785. In his experiments with carbon dioxide or fixed air, Cavendish demonstrated that this gas was produced by fermentation as well as by the action of acid on marble.

Cavendish also investigated electricity and thermochemistry, obtaining results that would have been revolutionary if they had been published during his life. In 1798, he presented a paper reporting the density of the earth as measured by a series of clever experiments.

The Cavendish Physical Laboratory was built as a memorial to Henry Cavendish by the seventh Duke of Devonshire.

J. FREDERIC WALKER

CELLULOSE

Cellulose, $(C_6H_{10}O_5)_n$, is a naturally occurring carbohydrate high polymer, hydrolyzable to glucose, and consisting of anhydroglucose units linked together to form long molecular chains. The cellulose linkage is beta-glucosidic, which distinguishes cellulose from alpha-glucosidic starch and glycogen. The molecular chains are essentially linear. In natural cellulose the number of anhydro-glucose units linked together (degree of polymerization) is typically 1000 to 3000, with a molecular weight of 160,000 to 480,000. Cellulose is a colorless solid of specific gravity about 1.50, insoluble in water and in all organic solvents.

Cellulose forms the skeletal structure of the cell walls (hence the name *cellulose*) in the woody portions of all plants. Here it is found imbedded in, or in part combined with, ligneous and other noncellulosic components of the plant. Cellulose also occurs in a relatively pure state in the stiffening fibers of grasses and reeds (such as flax and ramie) and in the seed hairs (cotton). It is a very common material, making up about one-third of all vegetable matter.

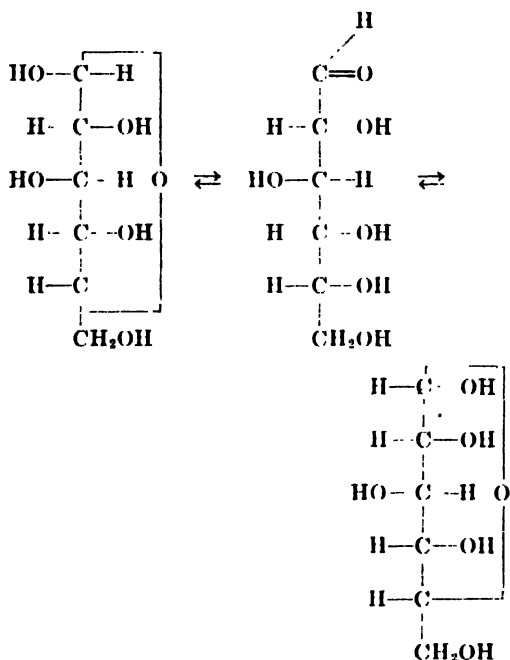
Wood contains 40-50% cellulose, 20-30% lignins, 10-30% hemi-celluloses and polysaccharides other than cellulose, and about 1.0% minerals in the form of ash. Cotton is a relatively pure natural

cellulose, containing only 3-15% of noncellulosic material.

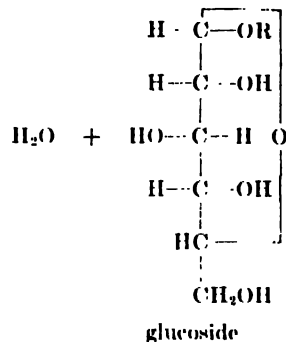
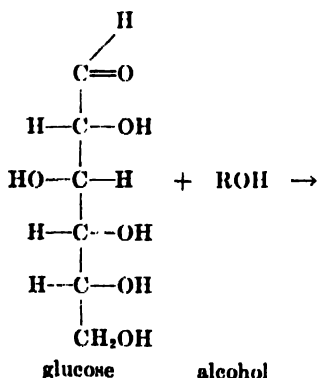
Wood cellulose which has been separated from impurities by chemicals is broadly spoken of as *woodpulp*. Recent practice, however, distinguishes between a *woodpulp*, defined as purified cellulose suitable for such purposes as the making of paper, and *chemical cellulose*, defined as cellulose which has been more highly refined and is suitable for the most exacting chemical uses. The complex noncellulosic substances co-existing with cellulose in wood have been termed *silvichemicals*, and the study of this field, *silvichemistry*.

Highly purified cellulose derived from cotton is termed *cotton pulp*, *cotton linters* or *linters pulp*. Cellulose fibers used in their natural form are termed *natural celluloses*. In this group are cotton, linen, jute, hemp, sisal and ramie.

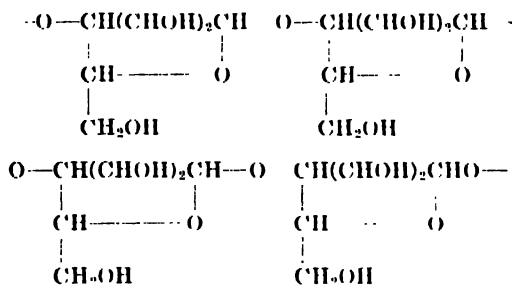
Cellulose may be thought of as a derivative of the six-carbon polyhydroxy alcohol, glucose, which exists in the tautomeric forms:



Glucose reacts with alcohols to form the hemiacetal or glucoside:



When the alcohol in the glucosidic reaction is another molecule of glucose, condensation from the number 1 carbon of one glucose to the number 4 carbon of the other gives a structure corresponding to the cellulose polymer:



Note that cellulose has the *pyranose* (six-membered) ring and that there are two secondary hydroxyls and one primary hydroxyl group available for chemical reaction.

Wood cellulose in North America is largely produced in the Pacific Northwest including Western Canada and Alaska (Western hemlock and spruce), in Eastern Canada and New England (Northern spruce and hardwoods), and in the Southeast and South (Southern pines). Wood cellulose is also produced in major quantities in the Scandinavian peninsula. The major processes used in chemical pulping are the *sulfite process* and the *alkaline processes*. The latter consist of the *sulfate (kraft) process* and the less-used *soda process*.

In mechanical pulping (*groundwood*), wetted wood is forced against a revolving stone and separated into fibers. The product is used in book-print and newsprint.

Sulfite digestion. After debarking, wood is cut into small chips and "cooked" at elevated temperatures and pressures in large pressure vessels or digesters. The cooking liquor is an aqueous solution of an alkaline-earth bisulfite, usually $\text{Ca}(\text{HSO}_3)_2$, plus excess SO_2 . The digestion primarily converts the lignins present into soluble lignosulfonates.

Sulfate digestion. The lignins are solubilized by cooking in an aqueous solution of NaOH plus Na_2S . Sulfur loss in the process is made up by the addition of Na_2SO_4 ; hence the name sulfate process.

Soda digestion. Aqueous NaOH is used as the cooking liquor.

Pulp purification. The pulps obtained from any of the above digestions are subjected to later stages of purification known as *bleaching stages*. In these the cellulose is both purified and decolorized. Yield following digestion is about 50%, following bleaching, about 40%.

Cotton linters pulp. To produce cotton pulp, cotton linters (short fibers adhering to the seed after ginning) are digested with caustic soda, washed and bleached. If the linters are to be sold in bulk form, the bleached fiber at this stage is mechanically fluffed, dried and baled for shipment. If sold in sheet form, the bleached fiber is formed into a continuous sheet on a paper machine, dried and cut into specified sheet sizes. Yield is about 75%.

Cotton fibers (seed hair from the *Gossypium*) are made up of concentric lamellae of spirally wound fibrils, with reversal of the wind at intervals. Wood fibers also have a well-defined macrostructure, with lamellae and sheathes. Wood fibers are about $\frac{1}{25}$ -inch long in hardwoods and about $\frac{1}{8}$ -inch long in softwoods, with over 142 million fibers per ounce of cellulose.

Cellulose derivative solutions are characterized by high viscosity. This viscosity is largely determined by the average degree of polymerization of the cellulose used in a given manufacturing process (D.P., equals the number of anhydro-glucose units per molecular chain). The viscosity may also be adjusted by a controlled chain-length shortening (degradation) carried out as part of the process itself.

Cellulose is commonly characterized by its *alpha*, *beta* and *gamma* cellulose content. Alpha-cellulose corresponds to material of high D.P.; beta and gamma-cellulose, collectively termed *hemicellulose*, are of lower D.P. Alpha-cellulose represents usable cellulose in the chemical manufacturing processes; hemicellulose may be in part lost and not appear as yield in the final product.

DEGREE OF POLYMERIZATION (D.P.)

Natural cellulose	3000
Cotton linters pulp	2000
Wood chemical cellulose	1000
Low-viscosity wood cellulose	700
Viscose rayon yarn	400
Acetate rayon yarn	250
Alpha cellulose	D.P. greater than 200
Beta cellulose	D.P. 10 to 150
Gamma cellulose	D.P. 10 or less

Cellulose is *polycrystalline*, that is, it is not in any sense a single crystal but consists of *crystalline areas* imbedded in *amorphous areas*. The crystalline areas are oriented and crystalline with respect to the cellulose molecules composing them and, in addition, the crystalline areas themselves may be oriented with respect to the gross fiber axis. To illustrate these terms, the cellulose molecules may be compared to a bundle of pencils. The pencils in the bundle are *oriented* if they are grouped in a parallel arrangement. They are *oriented and crystalline* if in addition each pencil is

rotated to have the same position with respect to its long axis, that is, if each pencil is rotated so that the side having the brand is uppermost.

Alternate terms used to describe cellulose polycrystallinity are *regions of high lateral order* and *regions of lower lateral order*. This nomenclature emphasizes the fact that cellulose is not sharply discontinuous, the transition from one degree of order to another being a gradual one.

Chemical reagents penetrate more easily into the amorphous areas than into the (more) crystalline areas. Swelling of the cellulose assists penetration.

Chemical reactions with cellulose are usually not expressible in stoichiometric relationships. The simplest explanation for this is that they are *topochemical*. On this basis they are straightforward chemical reactions, but can occur only with cellulosic reactive groups which are *available* in the amorphous areas or on the surfaces of the crystalline areas.

The polycrystalline relationships in cellulose profoundly affect cellulosic products (for example, rayon and cellophane) in such properties as water pick-up, flexibility and strength.

The principal chemical reactions of cellulose are (1) alkaline oxidative degradation resulting in chain length shortening, (2) acidic oxidative degradation with the formation of reducing groups and carboxyls (oxycelluloses, hydrocelluloses) and (3) derivative formation involving the active hydrogen atom on the cellulosic hydroxyls. The topochemical nature of most of these reactions should be emphasized. It may account for the failure of the past chemical literature to reduce the many soda cellulose, oxycellulose and hydrocellulose "compounds" to any stoichiometric pattern.

Cellulose Nitrates (Nitrocellulose $[R(ONO_2)_n]$) are formed by direct reaction with nitric acid. They are used as coating lacquers, military explosives (gun cotton), sporting ammunition (smokeless powder) and nitrate photographic film.

Carboxymethylcellulose, $[R(OCH_2COOH)_n]$ is produced by the action of chloroacetic acid on soda cellulose. It is used as a thickening, suspending and stabilizing agent.

Ethyl Cellulose $[R(OC_2H_5)_n]$, is manufactured by the reaction of ethyl chloride on soda cellulose. It is used as a synthetic gum and thickener.

Soda Cellulose (alkali cellulose, $R(ONa)_n$), is an intermediate formed by the action of aqueous NaOH on cellulose and used in the manufacture of cellulose ethers and viscose.

Cellulose Xanthate $[R(OCSSNa)_n]$, is produced by the reaction of CS_2 on soda cellulose. Cellulose xanthate is dissolved in aqueous NaOH to form viscose and is used in large tonnages in the manufacture of rayons and cellophane. Continuous-filament rayon yarns are used for knitwear and woven fabrics. Cut into short lengths, rayon *staple* fiber is used in rugs and carpets and as blending fiber in spun yarns. High strength rayons are used for tire cord.

Cellulose Acetate $[R(OOCH_3)_n]$, is produced by the action of acetic anhydride on cellulose. Cellulose acetate is used for textile yarns, for plastic

molding, for thin films competitive with cellophane and for acetate photographic film.

J. P. HOLLIHAN

Cross-references: *Carbohydrates, Textile Chemistry, Polymerization, Paper*

CEMENT, PORTLAND

Portland cement may be defined in many ways. To the layman it is something which is used for making concrete. The engineer thinks of it as the finely pulverized clinker resulting from the partial fusion of a carefully proportioned mixture of limestone and clay. The chemist might refer to it as consisting principally of a mixture of certain silicates, aluminates and ferrites of lime. The American Society for Testing Materials defines it as "the product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates," to which the addition of certain materials in limited amount is permitted.

Modern portland cement is made by the partial fusion, at temperatures up to 1500°C , of carefully designed and pulverized mixtures of calcareous material (limestone, chalk, shells, marl, etc.) and argillaceous material (clay, shale, blast-furnace slag, etc.). Other materials, as sandstone or iron ore, are sometimes added. Some constituents of these or other raw materials are known to give rise to undesirable properties in the ultimate concrete if present in excessive amounts, and so are rigidly limited by the standard specifications.

The rocks are first broken up in giant crushers and finally in ball mills to a very fine powder. The grinding may be accomplished in the dry state (dry process) or water may be added to bring the material into the form of a slurry (wet process). Sometimes excessive amounts of quartz or mica or other minerals are removed from the slurry by a flotation process or by passing a part of the slurry through a centrifuge. Excess water is removed in gravity settling tanks or various forms of classifiers, or it may be reduced by use of a vacuum filter.

The dry powder or slurry or filter cake is fed into one end of a huge slowly rotating steel-shell kiln that may be from 8 to 15 feet in diameter and from 100 to 500 feet long. The kiln is set at a slight inclination so that the rotation causes the contents slowly to travel down toward the discharge end. Heat is introduced at the lower end of the kiln. The kiln is lined with refractory brick, the hottest zone near the burning fuel consisting usually of a high-alumina or a magnesia base.

As the raw mixture travels down the kiln, water is first expelled, the heat exchange in wet-process plants usually being facilitated by chains suspended at the upper end of the kiln. Further down in the kiln the carbon dioxide is discharged from the limestone and other carbonates, organic matter is burned and volatile constituents are evolved. Here also some reactions take place by diffusion between constituents in the solid state. As the mixture enters the hottest zone at $1450\text{--}1500^{\circ}\text{C}$, some of the material is raised above its melting temperature, and up to 30% of liquid may be produced, forming pellets $\frac{1}{4}$ to 1 inch in diameter.

This clinker is dropped out of the kiln into a cooler which may consist of a rotating steel drum or an air-cooled grate or some other device for rapid cooling.

The cooled clinker is ground in ball mills, usually with gypsum to give about 1.5–2.0% SO_2 in the cement, to a fineness of about 1600–1800 sq. cm. per gram. Sometimes small amounts of an admixture is added for a special purpose, as to improve the grindability or to incorporate air for air-entraining cement, which is of improved durability, especially in northern climates. The resulting pulverized material is the portland cement of commerce. In Europe extensive use is made of blast-furnace slag and pozzolanic materials interground with the clinker in amounts varying from 15 to 85%.

Portland cement clinker has been found to consist principally of tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) and beta dicalcium silicate ($\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$) together with lesser and variable quantities of tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), tetracalcium aluminato ferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) or some solid solution of the iron phase, periclase (MgO), free lime (CaO) and trace amounts of many other compounds.

The specifications in use in the United States recognize five types of cement, the first three of which may or may not be air-entraining:

Type I, for use in general concrete construction when the special properties specified for types II, III, IV and V are not required.

Type II, for use in general concrete construction exposed to moderate sulfate action, or where moderate heat of hydration is required.

Type III, for use when high early strength is required.

Type IV, for use when a low heat of hydration is required.

Type V, for use when high sulfate resistance is required.

The properties of a cement in concrete have been found to be determined by the relative amounts of the several compounds it contains and its fineness. Consequently, the special properties indicated by the types as above defined are obtained by limitations imposed on certain compounds and on the surface area. Since tricalcium silicate reacts with water rapidly, and dicalcium silicate slowly, higher early strength is attained by increasing the former at the expense of the latter, and by finer grinding. And since tricalcium aluminate evolves a large amount of heat during its hydration, and also reacts rapidly with sulfates in solution, that compound is limited in cements requiring low or moderate heat of hydration and high-sulfate resistivity.

When cement is tempered with water, reactions proceed that result in a stone-hard paste; it is this paste that bonds the sand, gravel or crushed stone in the production of concrete. There is formed rapidly a saturated solution of calcium hydroxide and, more slowly, hydrates of the silicates and other constituents. The principal bonding agent is the calcium silicate hydrate, a colloidal gel that up to recent times has eluded all attempts at a precise understanding. But attacks by x-ray and

electron-optical methods have gone far to resolve its structure, which now appears to consist of crystalline spherical particles some 50-200 Å. in diameter.

The production of portland cement in the United States has increased from about 8 million barrels in 1900 to over 284 million barrels in 1953. A barrel of cement contains 376 lbs. or 4 bags of 94 lbs each.

R. H. BOGUE

CERAMICS, see CLAYS, REFRACTORIES

CEREAL CHEMISTRY

Cereal chemistry embodies a great deal more than the chemistry of the cereal grains. It starts with a study of the growth of the plants which produce the seeds, and continues with the production and the composition of the seeds, the chemical changes on storage, the refining of the grains for special purposes, the use of these products and their byproducts, the nutritional value of the whole kernel and its parts, and includes in its realm all products and processes which come in contact with the cereals. The work of a large number of cereal chemists is involved with the milling of wheat and with the use of the flour in the baking industry. To them, cereal chemistry involves the chemistry of yeast, milk, soybeans, bleaching, minerals, enzymes, etc., as well as of wheat. In the brewing industry, cereal chemistry must relate the chemistry of the barley to its ability to germinate, and the function of the malt, hops, yeast, and other ingredients to the fermentation and processing of the final beverage.

Of the various seeds, the cereal grains are perhaps the most important. There are a number of kinds of cereals and many varieties of each. It has been estimated that as many as 30,000 varieties of wheat exist, and over 12,000 have been identified. The six most important cereals are listed in the order of their world production in Table 1.

TABLE 1. ANNUAL PRODUCTION OF CEREALS (1952-1953)

Cereal	Pounds per Bushel	Millions of Bushel		Billions of Pounds	
		U. S. A.	World	U. S. A.	World
Wheat	60	1,299	7,295	78	437
Rice	45	107	7,940	5	357
Corn	56	3,279	5,625	184	315
Oats	32	1,260	4,195	40	134
Barley	48	226	2,746	11	132
Rye	56	16	1,600	1	90

The production of the individual cereals is rather unevenly distributed. The United States produces half the corn and one-third of the oats, China one-third of the rice, and Europe one-third of the rye. The production of wheat is almost universal and it is the most important cereal in international trade. During the last 15 years, the production of the wheat, rice, and corn has increased, whereas that of the other cereals has de-

creased. The term "corn" is frequently misunderstood, as the word itself is a synonym for grain. It is applied to the most common cereal in a given locality. Thus in the United States, maize is the most common cereal and is called "corn". In many parts of Europe, "corn" refers to rye, and in Scotland to oats. Corn is the most important crop in the United States, and more than one-tenth of the farm land is devoted to its culture. Corn and oats have relatively little value in the human dietary, as over 90% of each goes into the feeding of livestock. Barley finds its chief outlet in the manufacture of malt. By comparison with the nutritional uses, the industrial utilization of cereals as sources of chemicals is rather small.

Like all forms of living matter, the constituents of the cereal grain are very numerous and many are very complex. The composition of the kernels is dependent upon their genetic make up, the climate, and the composition of the soil. For comparative purposes, the gross analyses are given in terms of the water, protein, fat, fiber, soluble carbohydrate, and mineral. These components vary widely for each of the cereal grains, but by compiling a large number of analyses, characteristic compositions for the different types of cereals are noted. Representative analyses are given in Table 2.

TABLE 2. REPRESENTATIVE ANALYSES OF THE IMPORTANT CEREAL GRAINS, % OF TOTAL

Cereal	Water	Protein	Fat	Mineral	Fiber	Carbohydrate
Wheat	10.2	13.1	1.7	1.9	3.0	70.1
Rice	12.5	6.4	2.1	5.9	7.8	65.3
Corn	11.0	9.0	4.0	1.8	3.0	71.2
Oats	10.0	12.7	5.3	3.0	7.0	62.0
Barley	10.8	11.0	2.2	2.5	3.8	69.7
Rye	10.0	12.3	1.7	2.0	2.3	71.7

The kernels of grain may be divided into several parts. The hull is a protective layer and consists largely of fiber. The bran is the outer layers of the seed proper and is rich in protein and mineral. The endosperm is the largest portion of the seed and it is the store house for most of the starch and protein. The germ is the vital center of the seed and is relatively rich in fat, protein, vitamins, enzymes, and minerals. The composition of the various products obtained from the cereals is thus dependent upon the degree of separation of the component parts. In the milling of wheat, the flour obtained has more starch and less protein, fat, and mineral than the whole grains. The reverse is true of the bran and germ which go largely into animal feeds.

Water. The water of the cereals is present in two forms. The most abundant is held in multilayers by adsorption on the free amino groups and peptide bonds of the proteins. It is easily displaced by heating, and its concentration is dependent upon the atmospheric temperature and humidity. A small amount of moisture is closely bound to the grain and it cannot be evaporated without causing

marked alterations. The proper moisture content during storage of the seeds is important for the preservation of their vitality and usefulness.

Carbohydrate. Among seeds, the cereal grains are characterized by a relatively high carbohydrate content, divided into crude fiber and nitrogen-free extract. The former is that portion of the grain which is insoluble in 1.25% concentrations of both boiling sodium hydroxide and boiling sulfuric acid. The fiber content is highest in the seeds with large hulls, oats and rice (Table 2), and is composed of pentosans and cellulose. The oat hulls have a commercial value for the production of furfural by the reaction of sulfuric acid on the pentosans. The soluble carbohydrate or "nitrogen-free extract" is chiefly starch; it is the most abundant component of the seed, 50-70%, and is found chiefly in the endosperm.

Protein. Though the cereals grains usually are not considered a source of protein, they furnish about one-third of the human dietary protein in the United States, and in some countries the percentage is much greater. The cereals contain relatively less protein than the legume seeds and the protein has a poorer biological value. The concentration of the protein is determined from the nitrogen content. Thus the per cent nitrogen is multiplied by the factor 6.25. A factor 5.7 would be better for many of the cereal proteins, and, although it is sometimes used for wheat flour, the factor 6.25 has a much wider usage. The proteins are not evenly distributed throughout the seed. This is especially true in corn as portions of the endosperm are chiefly starch.

The cereal proteins are classified by their solubility properties. Each class may represent one or, more probably, many individual proteins. The crude water-insoluble protein of the cereals is known as gluten, and it includes up to 90% of the total protein. It is composed of two types, a prolamins which is soluble in 70% alcohol and a glutelin which is soluble in dilute acid or alkali. The solubility properties are used in their purification. Among the prolamins, gliadin is probably the same in wheat and rye, but hordein of barley and zein of corn have different amino acid components. Rice contains no prolamins, and its chief protein is a glutelin known as oryzenin. In wheat the glutelin is called glutenin. The ratio of the prolamins to the glutelin may vary for a given cereal and these proteins do not have the same physical properties when obtained from different grains. The gluten of corn does not form a sticky mass as does that of wheat, and so cornbreads are granular rather than porous. In wheat the gliadin is soft and sticky and is responsible for the binding, but the glutenin gives solidity to the gluten. Albumins and globulins are present in relatively small amounts, usually under 20% of the total protein. In general the proteins of oats have the highest biological value of any of the cereals, and it is possible to obtain a positive nitrogen balance with this cereal as the main source of protein. Additional nitrogen-containing compounds include nucleic acids and little studied nonprotein compounds as choline, betaine, amino acids, and traces of many others.

Fat. The fat of the cereals is found chiefly in the germ, with some in the bran, but very little in the endosperm. About 75% of the fatty acid present is of the unsaturated type, which results in an oily consistency. The germ oils of wheat and corn are available commercially and are used in the medicinal and table oil fields, respectively. Attempts are being made to increase the germ oil content of corn through genetics. This would also increase the biological value of the total corn protein. The acid number of the fat increases during storage and may be used as an index of the degree of soundness of the grain.

Minerals. The distribution of the minerals in the seeds approximately follows that of the oil. It was thought for a time that one of the advantages of whole wheat bread as compared to white bread was the larger amount of minerals it contained, especially phosphorus, calcium, and iron. It has since been shown that 75-85% of the phosphorus is present as phytic acid, the hexaphosphoric ester of inositol. The evidence indicates that the calcium and iron form insoluble salts with phytic acid so that these minerals cannot be utilized unless the complex is first hydrolyzed by phytase. Potassium, magnesium, and sulfur also form relatively large portions of the ash and many minerals are found in traces. The hulls of oats and rice are very high in silica, which accounts for the high ash content of these cereals (Table 2).

Enzymes. The cereal grains result as maturation of one generation of plant life. They are not inert. Their vitality may be expressed best in terms of the enzymes present. When called upon by favorable conditions, they initiate the changes which result in a new plant. Amylases, proteases, esterases, and oxidizing enzymes all play a role in supplying the new plant with food. The enzymic concentrations increase with the germination of the seed. Of the enzymes, the amylases, or diastase is of commercial importance. The brewing industry depends upon this group of enzymes in malt to produce maltose from starch so that the enzymes of yeast may produce alcohol. A certain amount of diastase should be present in flour for optimum baking qualities. Flour from intact grains will differ considerably in diastase content. The desired level is obtained by blending flours of different diastatic values or by the addition of small amounts of germinated wheat or barley. A small amount of sugar is normally present in the flour, and the diastase slowly liberates additional amounts for the yeast to ferment to produce the necessary carbon dioxide.

Vitamins. Vitamin A, which is found in plants as carotene, is not abundant in cereals. With the exception of yellow corn, the carotenoids of the seeds are not precursors of vitamin A so that the bleaching of flour can not be objected to on the grounds that this vitamin is destroyed. Vitamin D is not found in cereals and because of the adverse effect of phytic acid on the mineral metabolism, it is essential that adequate quantities of this vitamin be obtained from other sources. Vitamin E in the form of tocopherols is found chiefly in the germ, and is available from wheat germ. Vitamin C is not present in normal sound kernels, but it is

formed in relatively large amounts when the seeds germinate. The various B vitamins are the most important in the cereals. Large portions are removed in the extraction of flour and in the preparation of polished rice. Flour is now fortified with some of the vitamins lost in milling. The vitamins of rice may be partly transferred to the endosperm by cooking the cereal before processing it.

ALBERT A. DIETZ

Cross-references: *Proteins, Carbohydrates, Foods, Nutrition, Enzymes, Brewing, Vitamins, Fats, Enzymes*

CEREAL INSTITUTE

The Cereal Institute was organized in 1943 to promote the food value of breakfast cereals. This was to be done in a sound and conservative yet scientifically accurate manner and in cooperation with the National Nutrition Program. During the past years the Cereal Institute's program has been reviewed by leading government, educational, medical, and nutrition authorities and has received their approval and recognition.

The Cereal Institute conducts a continuous program of scientific research to study the harmful effects from the omission of breakfast and the beneficial effects derived from good breakfast habits. To date twenty scientific papers have been published on these studies in leading professional journals.

Each year studies are made of the food and breakfast eating habits of the public. These have disclosed that only one out of five children goes to school with a good breakfast; also well over half of the teen-agers and the adult population of the nation are not eating an adequate breakfast. With this as the background for the need of an educational program, the Cereal Institute offers to teachers and students in the schools a complete program of educational materials to improve breakfast eating habits. As a service to the consumer a home economics food editorial service is conducted conveying the findings of this research to the food editors and writers of America.

O. M. ANDERSON

CESIUM

Cesium, symbol Cs, is a soft, ductile, silvery-white alkali metal belonging in Group I B of the Periodic Table. Its atomic number is 55 and its atomic weight 132.91. The low melting point of 28.5°C makes cesium one of the three metals (with mercury and gallium) liquid at room temperature. This rare element was discovered by Bunsen and Kirchhoff in 1860 with the spectroscope. It ranks 40th in order of prevalence in the earth's crust.

Pollucite, an uncommon cesium aluminum silicate mineral found in pegmatites, is the chief source of cesium, although it is found as traces in certain salt and potash deposits. The ore is treated with acid, the silica dehydrated, and the cesium precipitated as a double chloride of lead ($2\text{CsCl} \cdot \text{PbCl}_2$) or antimony ($3\text{CsCl} \cdot 2\text{SbCl}_3$) by lead nitrate or antimony chloride, respectively. Cesium

chloride can be recovered from these compounds by hydrolysis which leaves CsCl in solution. The metal is formed from CsCl, m.p. 646°C, by reduction with calcium or by electrolysis.

Domestic production of cesium and its salts is only a few pounds per year. The price of the metal is \$4 per gram, and that of salts correspondingly high, i.e., \$2 per gram for CsCl and CsBr and \$3.50 per gram for Cs_2SO_4 .

The physical properties of cesium include: melting point, 28.5°C; boiling point, 705°C; density, 1.873 g/cc (20°C); specific heat, 0.06 cal/g (28.5°C); thermal conductivity, 0.05 to 0.065 cal/sec/cm²/°C/cm (28.5°C); latent heat of fusion, 3.766 cal/g; latent heat of vaporization, 146 cal/g; electrical resistance, 36.6 microhm-cm (30°C); viscosity, 0.609×10^{-2} poises (28.5°C); vapor pressure, 1 mm Hg at 278°C, 10 at 387°C, 100 at 515°C, and 400 at 635°C; and thermal neutron absorption cross section, 26 barns. Cesium is the most electropositive of the metals.

Chemically, the properties of cesium closely resemble those of potassium, differing in no outstanding respect. The hydroxide, CsOH, m.p. 272.3°C, is the strongest base known and must be stored in silver or platinum out of contact with air because of its reactivity with glass and CO_2 . Soluble cesium compounds include Cs_2SO_4 , CsNO_3 , CsCO_3 , CsOH, Cs_2S , and the halides, while CsClO_4 , Cs_2PtCl_6 , CsMnO_4 , and $\text{Cs}_4\text{SiW}_{12}\text{O}_{42}$ are relatively insoluble. The metal reacts vigorously with oxygen and water and must be protected from them.

Of limited industrial importance, cesium is used in scintillation counters, in photoelectric cells and infrared detecting instruments such as the "sniperscope," and as a "getter" in low-voltage vacuum tubes. In this last application the metal is usually produced in place by inserting a capsule charge of a salt plus a reducing agent, e.g. CsCl and Ca, into the tube and then heating the capsule with a high frequency source. Some cesium salts are used in the manufacture of mineral waters. Its use as a coolant in atomic energy applications is not promising because of its high thermal neutron absorption cross section, its scarcity, and its high cost, as compared with sodium or sodium potassium (NaK) alloys.

CLIFFORD A. HAMPEL

CETANE NUMBER

Cetane number serves as a means of comparing the ignition quality of diesel fuels. With all diesel fuels, a time lag occurs between injection of fuel into the cylinder and its initial combustion. Too long an ignition delay results in an excessively rapid pressure rise when combustion does occur and causes rough engine operation. Cetane numbers measure relative ignition delay (a high cetane number indicating a short ignition delay), thereby providing a basis for comparing the "smooth-running" characteristics of diesel fuels. Fuels of higher cetane number also permit cold starting at lower temperatures.

The cetane-number scale is based on blends of

two reference hydrocarbons—*cetane* (normal hexadecane), given a value of 100, and *alpha-methylnaphthalene*, assigned a value of zero. Fuels are rated by comparison with reference blends of these hydrocarbons under standardized test procedures (ASTM D-613) in a single-cylinder, variable-compression ratio, CFR (Cooperative Fuel Research) engine. The cetane number of a fuel is the percentage by volume of cetane in the reference blend that requires the same compression ratio as the fuel being tested for an ignition delay of 13 degrees crank angle. Calibrated secondary reference fuels are usually used for routine ratings.

The cetane number of diesel fuels is primarily dependent on their hydrocarbon composition, being high for fuels of low octane number and vice versa. For comparable distillate fuels, cetane number is closely related to API Gravity and fuel volatility, increasing with higher API Gravity and decreasing with higher volatility.

Ignition quality as expressed by cetane numbers can be improved by the use of additives, such as amyl nitrate. Although the specific effectiveness of amyl nitrate varies with fuel composition, a five cetane-number increase can be secured, on the average, by the addition of 0.13 per cent by volume of amyl nitrate.

Ignition-quality requirements are a function of engine design and operating conditions, and are primarily established for a specific engine by the need for good fuel ignition quality at light loads and low temperatures. Most modern high-speed diesel engines require fuels in the rather narrow range of 40 to 55 cetane number.

WHEELER G. LOVELL

Cross-references: *Octane Number, Petroleum*

CHARDONNET, LOUIS MARIE HILAIRE BERNIGAUD, COUNT OF (1839-1924)

Count Chardonnet was born in 1839 at Besancon, France. He studied chemistry at the Technical Institute at Besancon and at the Ecole Polytechnique. At the latter school he worked for some time with Pasteur, who was then investigating the silkworm disease that plagued the French silk industry. Chardonnet was interested also in the new technique of photography, and being a man of wealth, settled at his estate to devote himself to these interests.

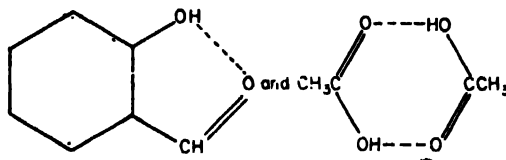
In 1855, Audemars has been granted a patent to produce artificial silk from cellulose nitrate. But Audemars drew his threads by dipping needles into the viscous solution. Subsequently, Swan made fibers from collodion by extruding them through a fine orifice. He used these fibers for lamp filaments. Chardonnet, who had also been working on this problem, produced nitrocellulose threads in 1878. He envisaged its enormous possibilities as an artificial silk and obtained a patent for the production of "Chardonnet silk" in 1884. His fabric created a sensation at the Paris Exhibition of 1889. In 1891 he started the first commercial plant to produce "Chardonnet silk" and production expanded rapidly into Belgium, Switzerland,

England and other countries. French insurance companies forced Chardonnet to improve his products, after it was found that his yarn was extremely flammable. In 1914 Chardonnet was awarded the Perkin Medal. His pioneering efforts in the establishment of the artificial fiber industry rightly earned him the title of "father of the rayon industry".

BERNARD JAFFE

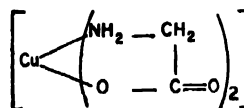
CHELATION

Chelation is the formation of a heterocyclic ring containing a metal ion, the metal being attached by coordinate links to two or more nonmetal atoms in the same molecule. The parent word "chelate" which is properly used as an adjective (e.g. chelate ring) and colloquially, as a verb and as a noun, is derived from a Greek word meaning "crab's claw", which refers to the tenacity with which the coordinating group holds the metal ion. The word was coined by G. T. Morgan and H. D. K. Drew. The terms "chelate" and "chelation" have been extended to refer to rings formed by hydrogen bonding, as in salicylaldehyde and acetic acid,



but this is not entirely justified, as the hydrogen atom does not form coordinate bonds with the two oxygen atoms simultaneously.

The importance of ring formation in metal coordination compounds was first established by Ley through a study of the copper (II) derivative of glycine. This compound is quite different from copper (II) acetate in that it is deep blue in color, and its solutions show little conductivity. These properties would seem to rule out the structure $\text{Cu}(\text{OOCCH}_2\text{NH}_2)_2$, and the structure $\text{Cu}(\text{NHCH}_2\text{COOH})_2$ is ruled out by the fact that N, N-dimethylglycine gives a similar product. Ley therefore considered the structure to be correctly shown by the formula



The most important property of chelation is found in the fact that it brings about a great increase in the stability of the bond between the metal atom and the coordinating group that forms the chelate ring. Monoamines are much poorer coordinators than ammonia, but complexes of the bidentate (literally, "two toothed" or "two clawed") ethylenediamine are many times more stable than those of ammonia, as shown below, where the logarithms of the stability constants of some ammonia complexes and ethylenediamine

complexes are collected:

Metal Ion	Log. Stability Constant	
	Ammonia Complex	Ethylenediamine Complex
Co ⁺⁺	5.3	10.7
Ni ⁺⁺	7.8	14.1
Cu ⁺⁺	12.6	20.1
Zn ⁺⁺	9.1	11.1

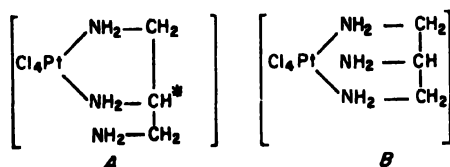
Similarly, complexes in which both ammonia and acetate groups are coordinated to the same metal ion are very much less stable than those containing the aminoacetate (glycinate) group.

This increase in bond strength is largely an entropy effect, and is shown primarily by the coordinate bonds between the metal and the donor atoms in the chelate ring, other bonds in the complex being affected only indirectly. Thus, the cobalt-ammonia bonds in the partially chelated

complex $\left[\text{Co} \left(\begin{array}{c} \text{NH}_2-\text{CH}_2 \\ | \\ \text{NH}_2 \quad \text{CH}_2 \end{array} \right)_2 (\text{NH}_3)_2 \right]^{++}$ are very

little different than those in the nonchelated $[\text{Co}(\text{NH}_3)_6]^{++}$. However, if the chelate ring has unusual steric properties, it may distort the entire complex and change the thermal stability or the chemical reactivity of all of the bonds.

Stability of the chelate ring is attained only when the ring size and other steric factors are right. It has been shown in many ways that with chelating agents containing only single bonds, the greatest stability is achieved when the ring consists of five members. For example, the complex formed between platinum (IV) chloride and α, β, γ -triaminopropane might have either structure A or structure B:



The fact that this complex is optically active indicates that the five-membered ring of structure A has been formed, the carbon atom marked with an asterisk thus becoming asymmetric.

The α -amino acids form much more stable complexes than do the β -amino acids; the corresponding γ , δ , and ϵ acids apparently do not form chelate rings at all. The α and β amino acids can be distinguished by the fact that the former react with cobalt (III) hydroxide to form deep-colored chelate complexes, while the latter do not. Ethylenediamine forms stable five-membered rings with many metals; trimethylenediamine $[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]$ forms much less stable six-membered rings, and the higher homologs $[\text{NH}_2(\text{CH}_2)_x\text{NH}_2]$ show almost no ability to coordinate. If two or three double bonds are introduced into the chelate ring, maximum stability seems to be shown when the ring consists of six members.

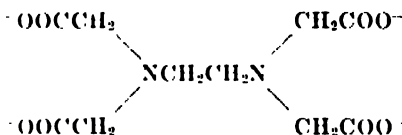
Four-membered rings are also known, and are illustrated by the familiar carbonate tetramine cobalt (III) complex $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$. Rings of seven, eight, and more members have been described, but most reports of such complexes are not adequately supported by proofs of structure. As the distance between donor atoms in the coordinating group increases, the tendency to ring formation decreases, and a tendency to form linear polymers becomes evident.

Complexing agents containing three or four or more donor atoms, all of which can coordinate simultaneously, are referred to as tridentate, tetradentate, or polydentate coordinators. When such complexers form fused chelate rings, the stability of the metal-ligand bonds is increased far beyond that achieved by simple chelate formation. This is called the "chelate effect" and is illustrated by the increasing stabilities of the complexes of ethylenediamine (one ring), diethylenetriamine (two rings), and triethylenetetramine (three rings), which is the more remarkable when it is recalled that secondary amines generally form much less stable coordinate bonds with metals than do primary amines.

INFLUENCE OF NUMBER OF RINGS ON STABILITY OF ZINC COMPLEXES

Coordinating Agent	Donor Atoms	Number of Fused Rings	Log Stability Constants				% dissociation of 0.001 M solution
			k ₁	k ₂	k ₃	k ₄	
NH ₃	1		2.4	2.4	2.5	2.2	7.7
NH ₂ CH ₂ CH ₂ NH ₂	2	1	5.9	5.2			1.2
NH(CH ₂ CH ₂ NH ₂) ₂	3	2	9.0				
N(CH ₂ CH ₂ NH ₂) ₃	4	3	11.6				1.4 × 10 ⁻⁴

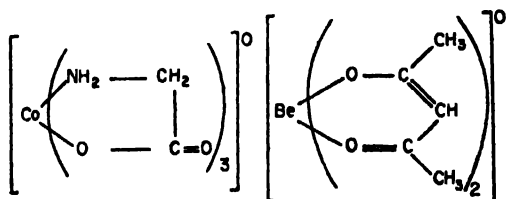
The chelate effect is strikingly illustrated by the complexes of the sexidentate ethylenediamine tetraacetate ion,



which can coordinate through both nitrogen atoms and all four carboxyl groups, forming five fused rings. In some cases it utilizes only two or three of the carboxyl groups, but even so, it is a powerful coordinator, and has found wide use as a sequestering agent.

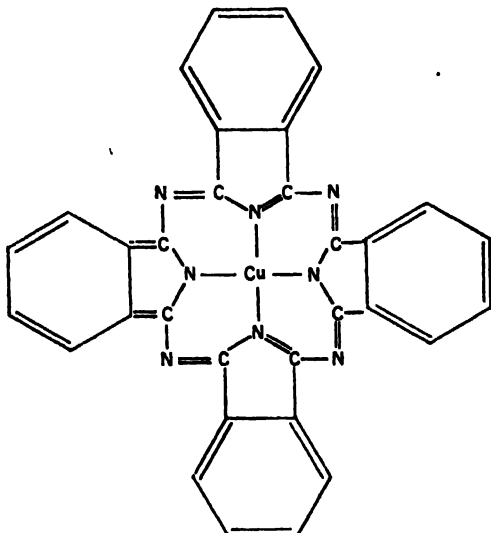
The charge which a complex bears is the sum of the charges on the coordinating groups and the metal ion from which it was generated. It may be either positive or negative, or it may be zero. The zero charge is usually achieved by the combination of a bidentate ligand bearing a single negative charge with a metal ion for which the coordination number is twice the oxidation number. Fully chelated complexes of this sort comprise a special class of compounds known as "inner complexes". Such compounds show greatly enhanced stability. Some of them are volatile, and most of them are insoluble in water, but easily soluble in nonpolar

solvents. They behave like organic substances. Nonchelated complexes of zero charge, such as trinitro-triammine cobalt (III) usually do not show these properties and are not considered to be inner complexes. The stability of the inner complex compounds is illustrated by tris-glycine cobalt (III), which can be recrystallized from hot, 50% sulfuric acid, and by bis-acetylacetone beryllium (II), which distills without decomposition at 270°C.



Many of the organic precipitants used in analytical chemistry are applicable because they form inner complexes; among these are 8-hydroxy quinoline, dimethylglyoxime, and nitroso- β -naphthol. In some cases, the metal in the resulting precipitates is determined by drying and weighing while in other cases the complex is extracted into an organic solvent and the metal is determined spectrophotometrically.

The fulfillment of the rules which lead to the stability of chelate rings is well illustrated by the amazingly stable copper phthalocyanine, which is not decomposed even at 500°C. In the phthalocyanine molecule we have an inner complex containing four resonating six-membered fused rings:



JOHN C. BAILAR, JR.

Cross-references: *Heterocyclic Compounds, Asymmetry, Sequestering Agents*

CHEMICAL DATING

The principal chemical methods of dating geological formations and artifacts are based on

the measurement of the end products of radiochemical changes or on the degree of residual activity of a radioactive substance; they yield absolute dates and are capable of rather wide application.

The oldest and most thoroughly investigated of the chemical methods is the estimation of the age of uranium minerals from a measurement of the amount of helium or lead they contain. Though a great deal of attention has been given to age determination from the measurement of helium content, it is now generally recognized that because of the tendency of this gas to escape, the helium method is always likely to yield results that are considerably in error. Hence the measurement of the amount of lead produced by radiochemical decomposition is the preferred method. If a pure uranium mineral has not been altered by leaching or weathering, the ratio of the percentage of lead it now contains to the percentage of uranium is an index of its age, which may be calculated from this ratio and the known disintegration rate of uranium. Likewise for a pure unaltered thorium mineral. If a mineral contains both uranium and thorium, the ratio of the percentage of lead to the percentages of uranium and thorium is still an index of its age, though now the calculation must take into account the different disintegration rates of uranium and thorium. A further complication and a possible source of serious error, arises if the mineral originally contained ordinary lead as an impurity. Fortunately, the presence of such lead may be detected by isotopic analysis with the mass spectrograph since ordinary lead contains the isotope Pb^{204} which is not a product of the radiochemical decomposition of either uranium or thorium, and a correction may be applied to the total percentage of lead in the mineral or to the percentages of the other isotopes of lead that are present. Instead of depending on the ratio of the percentage of total radiogenic lead to the percentage of uranium, thorium, or both, it is generally more accurate and more advantageous to depend on the ratio of the percentage of one or more of the individual lead isotopes to the percentage of the parent element or elements. However, because of the experimental difficulties of this method of analysis, most age determinations up to now have been based on the results of ordinary gravimetric analysis.

Although it is theoretically possible to measure the age of minerals containing a few naturally radioactive metals other than uranium or thorium, the only such measurement that has been applied practically as yet is based on the radioactivity of rubidium. Natural rubidium contains the isotope Rb^{87} which emits a beta particle to yield the strontium isotope Sr^{87} . The percentage of Rb^{87} in a mineral is determined by multiplying the percentage of rubidium found on analysis by the factor 0.27. The ratio of the percentage of strontium found on analysis to the percentage of Rb^{87} is the index of age, which may be calculated in the usual way from the known half-life of Rb^{87} .

For the determination of the time of occurrence of very recent geological events, for dating prehistoric human events, and for determining the

age of certain kinds of artifacts, the radiocarbon (C^{14}) method of Libby is the most generally useful chemical method available.

A fundamental assumption of the method is that the amount of cosmic ray activity, the composition of the atmosphere, and other conditions under which C^{14} is formed have remained constant for the entire period of time over which this method is applicable; in other words that the proportion of C^{14} in the carbon of living tissues has remained the same over this whole period.

The careful selection and preparation of the sample is an essential step for reliable dating by the radiocarbon method. Organic matter of more recent origin than the sample, such as plant remains or soil containing humus, must be removed, and care must be taken to remove all mineral matter containing carbon. In general, the sample must be cleaned physically to remove foreign matter, and as an additional precaution soaked for several hours in normal hydrochloric acid. After treatment with the acid, it is thoroughly washed with water and dried completely in an oven. Sufficient purified sample must be prepared to yield at least ten grams of elementary carbon.

The prepared sample is completely burnt to carbon dioxide in a suitable train, or if it consists of shell, is treated with hydrochloric acid of sufficient concentration to yield carbon dioxide. For combustion, oxygen is passed over the heated sample and the combustion products are passed over hot copper oxide to complete the combustion. In either case the resulting gas is passed through a dry-ice trap and a Drierite tube to remove water and is collected by condensation in a nitrogen-cooled trap. Since the product thus collected is usually contaminated with other condensed gases such as oxides of nitrogen and radon in traces, it must be purified. This is done by warming the condensate, passing the gas mixture into ammonium hydroxide solution, and adding a solution of calcium chloride to yield a precipitate of calcium carbonate. After washing thoroughly with distilled water, this should contain all the carbon of the sample in the form of pure calcium carbonate. This pure product is then treated with hydrochloric acid, using the same train as in the combustion procedure, and the evolved pure carbon dioxide is dried as before and collected as a gas in storage bulbs.

The next step is the reduction of the carbon dioxide to carbon. This is done in an iron combustion tube containing magnesium turnings mixed with about one per cent of cadmium turnings as a catalyst. The gas is passed at a moderate rate into the tube containing the hot metals until all the carbon dioxide has reacted. After cooling, the mixture of carbon, magnesium oxide, and unreacted metal is removed from the tube and placed in a large beaker. This mixture is then treated first with water and then with concentrated hydrochloric acid to dissolve everything but the carbon. The resulting solution is separated from the carbon by the use of a glass filter stick, and the carbon is repeatedly washed with hot distilled water by decantation, and dried. The carbon is then again

treated with hydrochloric acid, and filtered, washed, and dried as before.

The final step is grinding in an agate mortar to a uniform powder. The sample is then placed in a small bottle with a tight cap until the measurement of its activity can be made. In spite of the double acid treatment, the sample always contains some magnesium oxide. The percentage of this must be determined in a small part of the sample by combustion so that a correction may be made for this inactive material when the activity of the sample is measured and calculated.

In general, the error of age determination by the radiocarbon method is 5-10 per cent in the range where reasonable accuracy may be expected. This degree of error is not serious in dating geological or prehistoric materials or events, but is usually too large to give useful results for periods within the limits of human history. (See *Archaeological Chemistry*)

EARLE R. CALEY

Cross-references: *Radioactivity, Chromium, Lead*

CHEMICAL ECONOMICS

The chemical manufacturing industry has shown an unprecedented growth rate during the last two decades, and *synthetic* organic chemistry has grown four times as fast as the average of all American industry. Investment in chemical manufacturing facilities is approximately \$25,000 per worker in chemical manufacture and approximately \$100,000 in the petroleum and coal products industries. While population growth in the period of 1930-50 averaged only $\frac{1}{10}$ of 1% per year, the average growth rate of chemical industry over this period was 10% per year. In the period of 1939-52 the output of chemical process industries increased in sales volume from \$10 billions to \$50 billions; in 1952 the capital expenditures for chemical and allied products reached a peak of \$1.5 billion. From 1950-1955 the chemical industry spent over a billion dollars a year on expansion.

Investment in research in the U. S. in 1930 was about \$165 million. In 1940 the total research expenditures had risen to approximately \$350 million, about $\frac{1}{2}$ of 1% of the national income. In 1945 approximately \$1.1 billion was expended for research in the United States, with about half of this expenditure spent for military objectives. Research expenditures in chemical industry increased nearly tenfold in 1950. During Korean hostilities, between \$1.7 and 2.3 billion was spent annually, or approximately $\frac{3}{4}$ of 1% of the national income. This total research expenditure was distributed approximately 42% to nonmilitary research, principally industrial, and 58% to military research and development. Before World War II, expenditures for applied research were approximately 6 times those of basic research. Since then, the recognition of need for a greater availability of fundamental knowledge has initiated renewed interest in the broadening of basic areas of research and the restoring of a more effective balance between research devoted to immediate objectives and those of basic knowledge.

European countries have approached a more nearly equivalent distribution between these two research phases; Great Britain, for example, maintained a ratio of applied to basic research estimated at 1.2 to 1 before World War II. Applications research, which proved so profitable to industry and so important in the production of war materiel in the United States, rested to a considerable degree upon the fundamental research knowledge developed in other countries before the war.

The production of steel in the United States and the stability of this economically has frequently been considered a barometer of the economic health of the chemical industry. Steel production, on the other hand, has always fluctuated more widely than the general economy as a whole, and the earnings of the steel industry have been very erratic. Before 1941 the capacity of the steel industry exceeded by several times the average production. During the period 1941-1944, capacity and production were almost completely in balance with production of 80-85 million tons of steel; 1944-46 production capacity again exceeded production, and this situation occurred to a lesser degree during 1948. Since 1949, production and capacity of the steel industry have been growing at a nearly balanced rate to a quantity of slightly more than 110 million tons per year.

No single segment of the organic chemical industry has shown such phenomenal rate of growth during the past 25 years as the plastics industry. Plastics have increased in consumption by more than 95% in this period. In 1934 the total production of all synthetic resins combined was less than 100,000 pounds; in 1954 it was over 3 billion pounds. All the major generic families of commercial resins shared in this growth with the exception of the cellulose resins, which have held fairly consistent in demand during 1946-1954 in the range of 60,000 to 100,000 lbs. Vinyl resin (excluding polystyrene) production, including the plasticizers, modifiers, and filler materials, have exhibited the sharpest growth curve, changing in magnitude from less than 10,000 lbs in 1940 to about 460 million lbs in 1953. In addition 463 million lbs of styrene resins were manufactured and sold, of which about 65% were used for the molding materials; the balance was used for protective coatings and other uses.

A vigorous research and development program directed toward the understanding of the fundamental nature and properties of polymeric materials, as well as the development of new uses and application, has been the keynote of the industry. Industrial interest in polymers has originated from the ready availability of raw materials, many of which were formerly wasted by products from other chemical operations. The attractive appearance of articles, resistance to corrosion, the large availability of raw materials within the United States, the ability to maintain molded shape or size under stresses and extreme temperatures, resistance to weathering, rot, deterioration and fungus attack, fresh and salt water, acids, chemicals and salt have all contributed to acceptance.

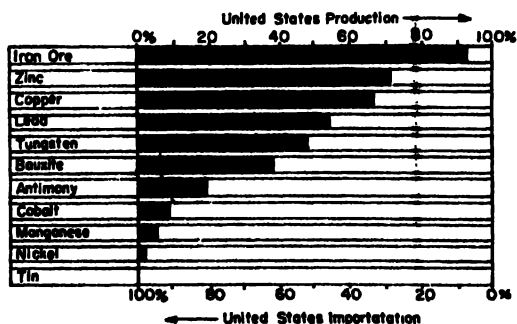
There is a constant rise in the consumption of

light, strong metals competitive with steel, for example, aluminum, which in 25 years has shown an increase in consumption from about 100,000 tons in 1929 to about 1.5 million tons in 1953. Magnesium has increased in production from 9,000 tons a year in 1941 to over 100,000 in 1952. As it can be economically extracted from sea water its supply is abundant. Some new metals possess special and unusual properties which make them attractive, in relatively small quantities, when added to steel. The need for a ductile material with a high melting point resulted in a use of molybdenum for jet engines. The most spectacular new metal is titanium. It is only about 6 years old as a commercially available pure metal, and, beginning near the zero point in availability in 1948, titanium production has increased to about 7,000 tons in 1954. Planned capacity now contracted for equals about 16,000 tons annually, and the Government has set a goal of 35,000 tons for 1957. The growth of titanium has been a forced and costly one, and has largely been subsidized by the Government as a vital defense need. Pure titanium has averaged about \$200 per pound until quite recently; although still very hard to obtain, it is currently selling at about \$100 per pound. Sponge titanium is more readily available at about \$5 per pound.

At the present time another new and extremely interesting metal has been developed—zirconium. It possesses excellent corrosion resistance and a very low neutron absorption which makes this metal of particular interest, when considering its light weight as well, as an ideal structural metal for nuclear reactors. It is currently selling at about \$10 per pound. It is still a precious metal, but the typical pattern of the industry is evident when one becomes aware that the cost of zirconium in 1948 was \$70 per pound.

Strategic Materials. Soaring demands, shrinking resources, and increasing pressure of rising real costs resulting from accelerated demand and war-time shortages have caused serious concern on the part of the government regarding the continued availability of basic strategic materials. The consumption of almost all materials is expanding rapidly and is pressing to an ever-increasing degree against available resources. The accompanying chart shows the rate of production and the rate of importation of our basic metal ores.

It can be noted here that no tin is produced in the United States and comparatively little nickel, manganese, or cobalt. The United States has had



to seek farther afield, in Labrador, to obtain substantial new deposits of iron ore; this is accompanied by constant improvement of methods for economically extracting the metal content of lower grade ores such as taconite. Handling of 0.6-0.7% copper ores was not considered in 1929; now such low content ores are in common use. In many cases these explorations and developments have been carried on by United States capital. An expanding chemical economy constitutes a problem for future generations as far as the consumption of strategic materials is concerned.

Types of Chemical Industry. The manufacturing chemical industry may be divided into two general classifications. The first comprises large-scale manufacture of tonnage quantity chemicals, where unit costs of labor and raw materials are low, but unit profit margins and continued profitability of the enterprise relies upon uninterrupted production in high-efficiency plants by *continuous processes*, and where transportation and distribution costs are low.

The second classification includes the "fine chemicals" and specialty items; these are manufactured normally in *batch processes*, with exacting quality specifications and control, at high unit costs of labor and materials. The limited market for these necessitates constant research expenditures to develop new uses. Chemicals in this category generally bear a high unit selling cost if they have a favorable competitive position and a strong patent structure. Costs of transportation and distribution, though high per unit quantity, are generally a lower percentage of the sales price per pound. The fluctuating stability of markets for these special chemicals is a constant threat to continued production, since research constantly under way in competing companies seeks to produce substitute and competitive products. If these are immune from the basic patent structure, made of cheaper raw materials, or show improved use in major industrial applications, they may completely replace the earlier product. Maximum flexibility in manufacturing plants for fine or specialty chemicals is necessary for economic health. The ability to adapt these plants promptly with a minimum of change to other products in demand in the fluctuating market must be incorporated into the basic design and layout of the plant.

The production of quantity or bulk chemicals requires large plants in order to maintain a strong competitive position, continuing markets, an uninterrupted flow of raw materials and well-developed distribution facilities. The large capital investment required for these continuous plants requires expanding new sources of external capital. The chemical industry traditionally has used internal funds to finance new plants; high post-war tax rates, particularly during the period of excess profits taxes, has sharply reduced the capital available from retained earnings. Problems of plant location in these large plants are particularly critical for efficient and profitable operation. The availability of adequate transportation facilities, sufficiently large areas for plant construction, substantial cooling water, and

adequate waste disposal facilities are among the essential factors.

GEORGE W. BLUM

CHEMICAL ENGINEERING

Chemical engineering is that branch of engineering which is concerned with the production of bulk materials from a few basic raw materials. The chemist works out the details of a given reaction in the laboratory, and the chemical engineer translates his work into large-scale plant operation. Typical examples of these bulk materials are industrial chemicals, gasoline, lubricating oils, rubber, soap, sugar, cement, metallurgical products, resins and plastics, synthetic fibers, and glass, to mention only a few. The producers of these materials are the chemical process industries, which now comprise the largest segment of all manufacturing enterprise in the United States. (See *Industrial Chemistry*).

Chemical engineering emerged as a separate branch of engineering when it was recognized that the chemical process industries employed a certain few basic operations in the manufacture of all their numerous products. These basic operations are called *unit operations*, and all chemical processing involves serial combinations of these unit operations together with some kind of chemical reactor. An understanding of these operations permits an intelligent attack on the technical problems relating to the production and refinement of any chemical product.

Unit Operations. The unit operations of chemical engineering are the basic physical operations common to all chemical processing. Among the more important are: fluid flow, heat transfer, filtration, evaporation, drying, distillation, mixing, gas absorption, solvent extraction, and adsorption. Fluid flow, heat transfer, and mixing are important in almost all chemical processing and are necessarily involved in the other unit operations, which are concerned primarily with separating constituents of mixtures. Fluid flow relates to the transport and metering of fluids; heat transfer relates to the transport of thermal energy between systems at different temperatures. Filtration is the operation of removing solids from a liquid by retention on a porous medium. In evaporation, solids are separated from liquids by boiling off the liquid. Drying is very similar, except that the proportion of liquid relative to solid is much smaller than in the case of evaporation.

Distillation is the vaporization and subsequent condensation of volatile liquids. When applied under proper conditions to mixtures of constituents which have different boiling temperatures, a separation of constituents results. Distillation is of particular importance in industries like petroleum refining, where the principal occupation is the separation of a complex mixture into a variety of products. Gas absorption is the removal of constituents from a mixture of gases by scrubbing the gases with a liquid which selectively dissolves out certain constituents. Solvent extraction is an analogous separation in which a

liquid mixture is contacted with an immiscible liquid solvent. In adsorption, a solid having an extended surface is added to a fluid mixture to adsorb selectively certain constituents in the mixture. Filtration is a mechanical separation, whereas all the other separations mentioned above involve the diffusion of a constituent from one phase to another. These *diffusional operations* may be treated by similar techniques, and for convenience they are often lumped together as *phase-change physical separations*. The latter name arises from the fact that the separations take place by a selective migration of constituents from one phase to another.

As an example of a typical process sequence, consider thermal cracking in a petroleum refinery. The preparation of the charge stock for the cracking involves distillation of the crude oil to separate it into various light cuts, intermediate cuts, and residuum. Selected high-boiling fractions make up the cracking feed stock, which is pumped to the cracking furnace through one or more heat exchangers wherein heat is exchanged with other oil streams. In the cracking furnace the charge stock flows at high velocities through many passes of pipes, which are heated by the flames in the furnace. After leaving the cracking still (furnace) the cracked oil is vaporized into a distillation column where it is separated into a variety of products including gas, gasoline, and recycle stock, i.e., stock having the same boiling range as the feed stock. In this particular process sequence the unit operations of fluid flow, heat transfer, and distillation are used both before and after the purely chemical step of cracking. It is typical of the chemical process industries that the unit operations comprise the bulk of the processing, while the purely chemical operations constitute only a minor part. (See *Cracking*.)

Unit Processes. Attempts to codify chemical operations in somewhat the same fashion as the physical unit operations led to the concept of the *unit process*. Typical unit processes are hydrolysis, pyrolysis, oxidation, halogenation, nitration, and sulfonation. Because of the wide variety of chemical behavior within a given unit process and because quantitative results are not possible this codification has not been as useful as the concept of the unit operations. (See *Reaction Rates, Catalysis*.)

Basic Principles. Although the introduction of the concept of the unit operations permitted the development of chemical engineering and the concomitant rapid technological advance in the process industries following World War I, recent trends in chemical engineering have made this concept unwieldy. Underlying the unit operations is a hard core of four basic principles which embrace every technical problem in chemical engineering. These principles may be identified simply as *conservation, equilibrium, kinetics, and control*.

Conservation. The conservation concept is an accounting concept which states that what goes into a system, if it is not transformed, must either accumulate in the system or come out of the system. Familiar examples are the law of conservation of matter and the law of conservation of energy.

These laws as applied to problems of fluid flow are the basis of the equation of continuity and Bernoulli's theorem, respectively. The conservation of momentum is another powerful tool in flow problems.

In phase change separations material balances account for matter and heat balances account for energy. In chemical reactions the material balances must be based on atoms or total masses.

The economic balance accounts for money and is of strategic importance in gaging actual performance or projected possibilities.

Equilibrium. Physical and chemical processes cannot go beyond the limits set by equilibrium conditions; hence a clear understanding of these conditions is essential to sound process engineering. In diffusional operations such as distillation, solvent extraction and the like, the degree of difficulty of separations and therefore some idea of the costs involved can be determined from the number of *equilibrium contacts* required for the separation.

The feasibility of chemical reactions as well as physical processes can be assessed from equilibrium relations. Furthermore, as will be seen, the driving forces for both physical and chemical processes are given by the appropriate displacements from equilibrium. Problems in kinetics can be handled meaningfully only when the equilibrium conditions are known.

Kinetics. By kinetics is meant time dependent processes or changes. A synonymous term is rate process, and in chemical engineering only four rate processes are of any great importance at present, namely, the physical rate processes of *momentum transfer, thermal transfer, and mass transfer*, on the one hand, and chemical rate processes or chemical kinetics on the other. All these rate processes involve a flow or transport resulting from a gradient in the appropriate potential. Momentum is transferred by velocity gradient; heat by a temperature gradient; mass by a concentration gradient; and chemical species by a gradient in chemical potential. In each case the total potential gradient is given by the total displacement from equilibrium, and in each case the rate equation is given by the product of a rate coefficient or reciprocal resistance and the driving force for the process.

Momentum transfer is the basic rate process in fluid flow; thermal transfer is the basic rate process in the various heat transfer operations; and mass transfer is the basic rate process in the phase change physical separations.

Control. Intelligent application of the principles of conservation, equilibrium, and kinetics permits the design and performance analysis of processes and equipment insofar as sizes and capacities are concerned. However, these principles of themselves give no picture of the behavior of processes under dynamic operating conditions. Since the dynamic behavior of processes strongly affects the yield and quality of products, a fourth basic principle must be added to handle problems relating to quality of operation. This fourth principle is one of *control*, since it necessarily relates to the character of performance of regulated

operations and equipment. (See *Automatic Process Control*.)

In a broad sense control may be defined simply as regulation for purpose. For chemical engineering applications three characteristics of control are of special pertinence:

(1) A *systems approach* must be used in appraising problems, that is, the entire system must be viewed as a whole, since the overall dynamic performance depends on every part of the system.

(2) In general only *feedback control* (closed-loop control) is economical. With this type of control the controller is continually apprised of the results of its action, and its subsequent actions are taken on the basis of the appraisal.

(3) Because of the feedback the over-all control system can become unstable; hence the limiting condition of *stability* provides an important first criterion of controlled performance.

As examples of how the four basic concepts of chemical engineering are utilized consider the following situations. In preliminary surveys the equilibrium concept identifies feasible and unfeasible process schemes. In gross process evaluations the conservation concept gives the gross amounts of materials, energy, and money that may be involved. In more detailed evaluations the kinetic concept in conjunction with conservation and equilibrium fixes sizes and capacities of equipment. The final kind of operation achieved by the process units is determined by the control concept applied with all the other three basic concepts.

In all engineering problems economic practicality is the overriding consideration, and factors of human relations frequently bear on decisions; but the purely technical aspects of chemical engineering problems can be handled via various combinations of the four basic concepts of conservation, equilibrium, kinetics, and control.

ERNEST F. JOHNSON

CHEMICAL LITERATURE

The literature of chemistry is voluminous. Some indication of the extent of chemical publication is to be found in the fact that by the end of its fiftieth year (1956) *Chemical Abstracts* will have published over two million abstracts of published chemical papers and patents. Inasmuch as *Chemical Abstracts* undertakes to cover the field of chemistry completely, counts of abstracts do provide a pretty accurate measure of the chemical research activity of the world. Growth in chemical literature is now rapid. Over recent years the increase has been about 10% per year. *Chemical Abstracts* published 8000 abstracts during its first year (1907); in 1954 it published 78,889.

Of the limited amount of information which can be stored effectively in the human brain, it is very desirable that a part consist of a thorough knowledge of how to obtain such recorded information as may be required from time to time. Skill in the library is valuable just as is skill in the laboratory.

In chemistry more than in any other field organized means of making the published literature available have been provided. Some of these tools

for the use of the literature of chemistry will be briefly discussed below. A good deal of pioneering in the publication of abstracts, indexes, and the like has been done in the chemical field.

Before discussing the kinds of chemical publications and describing or listing some of the specific books and periodicals, mention should be made of certain developments which are the outcome of a growing realization of the importance of having the rapidly accumulating information approachable and usable.

Many universities now teach courses in chemical literature and several text books or reference books are available. The best established of these are:

- (a) Mellon, Melvin G.: "Chemical Publications", New York: McGraw-Hill. 1928; revised ed., 1956.
- (b) Soule, Byron A.: "Library Guide for the Chemists", New York: McGraw-Hill, 1938.
- (c) Crane, E. J. and Patterson, Austin M.: "A Guide to the Literature of Chemistry", New York: Wiley & Sons, Inc. 1927; revised by Eleanor B. Marr, 1957.
- (d) Dyson, G. Malcolm: "A Short Guide to Chemical Literature", London: Longmans, Green & Co. 1951.

Since 1949 the American Chemical Society has had a Division of Chemical Literature. This is a very active division which meets twice annually for the presentation of papers and organized symposia. The Division has a small journal known as *Chemical Literature*.

In recent years there have been several congresses, most of them international, organized for the discussion of the problems of dealing with chemical literature. Some of these have been sponsored by UNESCO, some by the International Union of Pure and Applied Chemistry (IUPAC), and some by national groups, such as the Royal Society in England. The International Council of Scientific Unions has organized an International Abstracting Board for the purpose of helping abstracting services in science in avenues where international cooperation is possible. Chemistry is included in this effort. The latest international gathering was the First International Congress for the Documentation of Applied Chemistry, organized under the auspices of IUPAC, and held in London in November of 1955.

Periodicals. The journal literature constitutes much of the scientific source material. There are now over 6000 scientific, technical, or trade periodicals which publish original papers of chemical interest (the results of experimental investigation). These vary from such productive publications as the *Journal of the American Chemical Society*, which publishes approximately 1500 original chemical papers plus a number of briefer communications in a year, to publications of fields not primarily of chemical interest, but which use chemistry occasionally so that the publications are of chemical interest, though only infrequently so.

Many of the nations of the world have national chemical organizations the publications of which constitute the more important sources of original

chemical papers. Listing these would hardly be appropriate here. Good sources of information concerning scientific, technical, and trade journals of chemical interest are:

- (a) The List of Periodicals Abstracted by *Chemical Abstracts*. Washington, D. C.: The American Chemical Society. Revised ed. 1956.
- (b) *Periodica Chimica*. Weinheim, Ger.: Verlag Chemie, G.m.b.H. 1952.
- (c) "World List of Scientific Periodicals (1900-1950)", New York: Academic Press, Inc. 3rd ed., 1952.

In addition to original papers the periodical literature of chemistry is a source of abstracts, indexes, reviews, bibliographies, news, and statistics and other trade information.

Abstracts and Indexes. Of special importance in dealing with scientific literature are the abstract journals. These, with their indexes, are designed for the specific purpose of keeping the scientists in each of a variety of fields informed as to current developments and for making searches back through the literature possible.

Chemisches Zentralblatt was the first chemical abstract journal. This publication, started in 1830 under the name *Pharmaceutisches Centralblatt*, is still appearing and thriving, though it was discontinued for a short time because of World War II. It is comprehensive and well indexed, particularly for those who like a so-called systematic index, with effectiveness as a key somewhat lessened by considerable classification.

In the English language abstracts appeared during the years 1871-1925 in the *Journal of the Chemical Society*, during 1882-1925 in the *Journal of the Society of Chemical Industry*, and from 1906 to 1953 in a combination of these, first called *British Chemical Abstracts* and then, after being known as *British Chemical and Physiological Abstracts* during the period 1938-1944, called *British Abstracts* till it was discontinued at the end of 1953. These journals have published good abstracts, but they have not been quite complete in their coverage of the chemical field and their indexes have been less extensive than have some others.

The principal abstracting journal for chemistry now appearing in the English language is the American Chemical Society's *Chemical Abstracts* (1907-date). This journal has long striven to cover the field of chemistry, both pure and applied, completely (it published 78,689 abstracts in 1954), and it has also undertaken to publish a thorough key to the information in the abstracts in the form of scientifically prepared indexes. *Chemical Abstracts* publishes author, subject, molecular formula, organic ring-system, and numerical patent indexes, both annually and at ten-year periods. The indexes, considered together, require about 700 words to every 1000 words used in the publication of the abstracts.

Beginning in January, 1956, the office of *Chemical Abstracts* is to be spoken of as conducting the Chemical Abstracts Service and a research department in the new building of *Chemical Abstracts* on the Ohio State University campus in Columbus

will aid in working up additional means of helping chemists in dealing with the literature of their field.

For many years, starting back as early as 1858, *Bulletin de la société chimique de France* published abstracts, but this service was discontinued at the time of World War II, and now in France the whole field of natural science is reported briefly in the *Bulletin analytique*. Very brief descriptive abstracts, little more than annotations, are published, and there are no indexes.

An abstract journal is being published in Japan known as *Complete Abstracts of Japanese Chemical Literature* and a series of abstract journals was started in the Soviet Union in 1953. One of these publications (*Referativnyi Zhurnal, Khimiya Referaty*) is devoted to chemistry and it is making a good beginning.

There are many other sources of abstracts, some of them for limited fields and for limited periods of time, and some of them for fields which are only partially of chemical interest. Some journals which publish original papers also carry abstracts for their fields as, for example, the *Journal of the American Leather Chemists' Association*. Both for journals publishing original papers and for those publishing abstracts a list, with descriptive matter for the most important ones, is to be found in the Crane-Patterson "Guide to the Literature of Chemistry".

Patents. To many chemists, particularly those in industry, patent specifications constitute a valued source of new information. Much of the chemical work done in industrial laboratories and a great many of the products of chemists of inventive ability are reported and described in patent form only. Patents are searched also by chemical firms for information of legal and business significance. In the United States about one patent in five is now of chemical interest.

Most of the countries of the world with any degree of industrial development issue patents. Patents taken out in one country may be taken out also in another so that there is duplication of information published in the form of patent specifications.

Patent information can be obtained from (1) the original specifications (about 25 countries now publish full specifications), (2) official patent office journals, where abstracts or otherwise abridged specifications, sometimes only a list of claims, are given, (3) abstract journals, (4) scientific and technical journals which often discuss at length individual patents considered to be of special interest to their readers, (5) patent digests and lists, (6) court records, (7) publications on patent law and practice, and (8) periodicals devoted exclusively to the patent field.

In examining a patent for new chemical information it is well to bear the following in mind. In writing a patent application, the patent lawyer prepares a full description of the invention, as required by law. This description must be characterized by plenty of details. Frequently, though not always, a description includes several separate, numbered "examples" illustrating various aspects of the invention. The new technical

information is to be found in this detailed description of the invention together with the "examples", if any, not in the claims nor in the introductory, more general discussion of the nature or objects of the invention.

Usually the best place to do patent searching is in the patent office of one's country, such as the U. S. Patent Office in Washington, D. C., but a number of libraries have good collections of patent specifications. An outstanding collection of patent specifications is to be found in the New York Public Library, New York City.

A good source of information concerning the various patent office journals is the *Manual of Foreign Patents* written by B. Severance and distributed by the Patent Office Society, Washington, D. C.

Other Sources. Aside from the more or less regularly appearing periodicals and patents as sources of new information of interest to the chemist, there are numerous somewhat irregular publications, such as government bulletins and circulars, trade literature, annual reviews, reports by research organizations, dissertations or theses, bibliographies, privately published addresses or lectures, preprints and reprints, and personal correspondence.

In addition, useful information is sometimes to be found only in unpublished reports, such as the numerous wartime or peacetime national-defense reports provided by governmental research agencies. Much investigational work is done for governmental departments by outside contracts as well as within governmental laboratories. Some of the reports, classified at first, are later declassified and made available. This kind of report includes papers captured during wartime. A good source of information concerning these reports is U. S. Government Research Reports (formerly *Bibliography of Technical Reports* and before that *Bibliography of Scientific and Industrial Reports*) (1936-date), issued by the Office of Technical Services, U. S. Department of Commerce. This often gives a good deal of information in the form of abstracts and it provides information on how to get photoprints of these unpublished reports. The essential information in many of these reports eventually gets into the journal literature.

The government bulletins and the like may come from federal, state, or municipal governments. The State Agricultural Experiment Station bulletins are good examples. Municipal reports are likely to concern such municipal problems as those dealing with water supply and sewage disposal. Some of the federal government bureaus are quite productive of published research results. Many of the larger libraries receive all or most of the government publications.

The trade literature includes house organs, which may contain considerable new information not issued for advertising purposes, or not completely so, booklets which are useful even though issued primarily for advertising, and out-and-out advertisements.

Annual catalogs are a useful part of the trade literature. Good examples are the "Chemical Engineering Catalog" and the "Chemical Materials

Catalog", both published by the Reinhold Publishing Corporation, New York, N. Y.

Books. Chemical books, so important to the chemist, are being discussed last because, as a rule, they follow the journal and much of the other literature in appearance. While some books do report new information (the results of experimental investigation not previously published), ordinarily books are based on information which has already been in print, usually in periodicals. Authors customarily gather the published information on a given subject, classify it, and present it in readable and in more or less exhaustive form. Books are useful in teaching or learning, as a convenient means of reviewing a subject, and as a factor in some phases of literature searching. They introduce the novice to a more or less general subject or field; often they explain new theories in the light of facts already known, and they help to coordinate and systematize knowledge. Popular books of science are helpful in widening interest and support, and they make for better public relations. When the writer of a book has had long experience in a given field he is often able to interpret advantageously the more or less scattered investigational results which have originally appeared in the journal literature.

Many books offer convenient starting points in literature searches and reference books not infrequently provide ending points in certain kinds of searches, particularly when single bits of information are needed. A good reference book cites its authorities and serves as a guide to original articles.

Scientific books take various forms. They may be just general books, such as textbooks, but also they may be encyclopedic works, treatises of a broad scope, indexes, dictionaries, tables of constants, and pocket books. Some, such as encyclopedias and broad treatises, may consist of several volumes. Current and more recent encyclopedias are:

Thorpe's "Dictionary of Applied Chemistry" (Fourth Edition, 12 volumes, London: Longmans-Green, 1937-1954).

"Dizionario di chimica generale e industriale", by M. Giua and C. Giua-Lollini (3 volumes. Turin: Union Tipografico, 1948-1950).

Villavecchia's "Dizionario di merceologia e di chimica applicata", (Fifth edition, 4 volumes. Milan: u. Hoepli, 1949).

"Kingzett's Chemical Encyclopedia" (Eighth edition by R. K. Strong. London: Bailliere-Tindall and Cox, 1952).

"Encyclopedia of Chemical Technology", edited by R. E. Kirk and D. F. Othmer (14 volumes. New York: Interscience Press, 1947-1955).

"Encyclopedia of Chemical Reactions", (7 volumes), Jacobson-Hampel, New York: Reinhold, 1947-56.

A number of older encyclopedic works of chemical interest are to be found on library shelves.

General treatises or handbooks on chemical subjects are too numerous to be listed here. The compilation and publication of books of the "Handbuch" type has been particularly common in Germany through the years. There is a growing

tendency to publish annual review volumes in other countries, including the United States, in recent years. The general treatises of greatest general value to the chemist are Gmelin's "Handbuch der anorganischen Chemie" (Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse, Germany) and Beilstein's "Handbuch der organischen Chemie" (Springer, Berlin, Germany).

Gmelin, now in its eighth edition (started by R. J. Meyer and being continued by Erich Pietsch), is a lineal descendant of Leopold Gmelin's "Handbuch der theoretischen Chemie" (1817-1819). The eighth edition, with supplements to be completed by 1963 or 1964, will exhaustively cover inorganic chemistry for the period 1750-1950.

Beilstein, now in its fourth edition, edited by Bernard Prager and Paul Jacobson, was originally the work of Friederich Konrad Beilstein, a tremendous worker, who issued his first edition in 1881-1883, his second edition in 1886-1890, and his third in 1892-1899. The main series of the fourth edition includes all organic compounds of known structure to 1910. The first supplement to the fourth edition covers the period 1910-1920. The second supplement started publication in 1941 and will cover the years 1920-1930; it will soon be completed. A third supplement has been announced to cover 1930-1950.

Other important comprehensive works will be referred to here by author name only. They are (for inorganic chemistry) (1) Mellor, (2) Pascal, (3) Snelled, Maynard, and Brasted, (4) Abegg, (5) Dummer, (6) Doelter and Leitmeyer, (7) Evans, (8) Friend, (9) Moissan, (10) Huckel, and (11) Stähler; (for organic chemistry) (1) Elsevier, (2) Grignard, (3) Heilbron, (4) Groggins, (5) Houben-Weyl, (6) Rodd, (7) Whitmore, (8) Weissberger, (9) Velluz, (10) Vogel, and (11) Wagner and Zook; (for chemical methods and reactions) (1) Adams, (2) Theilheimer and (3) Jacobson. In this connection mention should be made of the series of books (the editors vary) called: (1) "Inorganic Syntheses", and (2) "Organic Syntheses". Many other very valuable and useful book or series of books could be added for more or less specific branches of chemistry, as Abderhalden's "Biochemisches Handlexikon".

Indexes which appear in the form of books have been provided for convenient consultation. In chemistry the more useful of these have taken the form of formula lexicons of which the following are very useful. Richter's "Lexikon der Kohlenstoffverbindungen", the first edition of which appeared in 1884 and the third edition of which brings the literature down through 1909 (Voss, Leipzig, 1910-1912), was followed by Stelzner's "Literature-Register der organischen Chemie" (5 volumes, Verlag Chemie, Berlin, 1913-1926), which covers the period 1910-1921. The formula index to Beilstein (fourth edition) covers the literature through 1919. For inorganic chemistry there is Hoffmann's "Lexikon der anorganischen Verbindungen" (3 volumes, Barth, Leipzig, 1912-1919); it covers the literature to April, 1909.

Chemical Abstracts started its annual formula indexes in 1920 and *Chemisches Zentralblatt* began its formula indexes of organic compounds in 1925.

There is a collective formula index to *Chemical Abstracts* for the period 1920-1946, and ten-year formula indexes will follow.

"The Ring Index" by Austin M. Patterson and Leonard T. Capell and the "Color Index" by Rowe for dyes are good examples of indexes in book form. The indexes to some of the abstract journals, such as *Chemical Abstracts*, are so extensive as to require binding in volumes separate from the abstracts, and some of the collective indexes involve several volumes.

Monographs (rather full treatises on special topics) usually give the detailed information that is needed by the research worker and are yet of convenient and relatively inexpensive size. These are frequently issued as parts of a series. Of special interest to the American chemist are the monographs on pure and applied chemistry sponsored by the American Chemical Society and published by the Reinhold Publishing Corporation.

In the chemical field, there are several dictionaries and glossaries (word books) which consist of definitions of words or terms all in one language and also there are chemical dictionaries for two or more languages written for the purpose of helping in the reading and translating of scientific and technical publications. A few of the more helpful chemical dictionaries in the English language are listed below.

"Condensed Chemical Dictionary", F. M. Turner (editor), Arthur and Elizabeth Rose (compilers) 5th edition, New York, Reinhold, 1956.

"Concise Chemical and Technical Dictionary", by Harry Bennet. New York, Chemical Publishing Co., 1947.

Gardner's "Chemical Synonyms and Trade Names", 5th edition (revised by E. I. Cook) England, Technical Press, 1948.

"Chemical Dictionary", by Hackh and Grant. 3rd edition, Philadelphia, Blakiston, 1944.

"Chemical Trade Names and Commercial Synonyms, A Dictionary of American Usage", by Williams Haynes, New York, Van Nostrand, 1951.

Henderson's "Dictionary of Scientific Terms", 5th edition (edited by J. H. Kenneth), Edinburgh, Oliver & Boyd, 1953.

"Chemie-Lexikon", by H. Roempp, 2nd edition in 2 vols., Stuttgart, Franckh'sche Verlag, 1950-1951.

Van Nostrand "Chemist's Dictionary", edited by Honig, Jacobs, Lewin, Minrath and Murphy, New York, Van Nostrand, 1953.

Very helpful in translating are:

"A German-English Dictionary for Chemists", by Austin M. Patterson. 3rd edition, New York, Wiley & Sons, 1954.

"A French-English Dictionary for Chemists", by Austin M. Patterson. 2nd edition, New York, Wiley & Sons, 1954.

"German-English Technical Dictionary", by Kurt F. Leidecker. Vols. I and II, New York, S. F. Vanni, 1951.

"Russian-English Technical and Chemical Dictionary", by Ludmilla Ignatiev Callahan.

New York, Wiley & Sons; London, Chapman & Hall, Ltd., 1947.

"Chemisches Fachwörterbuch, Deutsch-Englisch-Französisch", by A. W. Mayer. Vol. 1, Leipzig, Verlag von Otto Spamer, 1929.

The chemist is frequently helped by books of constants. The assembling of numerical data from the widely scattered original sources is a kind of service for which there is a good deal of need. The three most comprehensive works of this sort are:

- (1) "International Critical Tables", edited by E. W. Washburn, in 7 volumes and an index, McGraw-Hill, New York, 1926-1933.
- (2) Landolt-Börnstein's "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik" (6th edition of Physikalisch-chemische Tabellen), edited by E. E. Fucken, started publication in 1950 by Springer (Berlin) with four volumes announced.
- (3) "Tables annuelles de constants et données numérique de chimie, de physique et de technologie", twelve volumes which, published in 1912-1939, cover the years 1910-1936.

Scientists and engineers often find it useful to have at hand so-called pocket books, sometimes referred to as handbooks. In these are assembled miscellaneous information in convenient and readily available form. Good examples are:

- "Handbook of Chemistry and Physics", edited by C. D. Hodgman. Cleveland: The Chemical Rubber Co., Cleveland, O.
- "Handbook of Chemistry", edited by N. A. Lange, Sandusky, Ohio: Handbook Publishers, Inc.
- "Chemists' Yearbook", edited by E. Hope. Temperley, England: St. Ann's Press.
- "Kurzes Handbuch der Chemie", edited by Waldeman Koglin. Göttingen, Germany: Vandenhoeck and Ruprecht.

A classified list of reference books has been compiled for the Crane-Patterson "Guide to the Literature of Chemistry".

About two thousand new books of interest to the chemist now appear annually. There are various ways of learning of new chemical books as well as of acquiring information concerning the older books when this information is needed. Many scientific journals publish book reviews of interest to their specific fields and (or) lists of new books. Some of the abstract journals list new books in comprehensive manner. Publishers' catalogs can be obtained and watched. Some libraries keep files of such catalogs. The same can be said of catalogs of book dealers. Library accession lists can be obtained at little or no cost. The Library of Congress Lists are comprehensive. The New York Public Library issues a bimonthly known as *New Technical Books*, and the Carnegie Library of Pittsburgh, Pa., has a quarterly annotated list entitled "*Science and Technology: A Record of Literature Recently Added to the Carnegie Library*". Then there are general book guides such as *Publishers' Weekly*, *The Cumulative Book Index*, and *Technical Book Review Index*.

Library catalogs and book lists such as those

issued by ASLIB (the Association of Special Libraries and Information Bureaux of London) are still other means of learning about books.

Indexes. Indexes were briefly mentioned above as examples of a kind of book. From another viewpoint indexes deserve discussion here. There are various kinds of chemical indexes. The commonest kinds are devoted to (1) authors, (2) subjects, and (3) molecular formulas. The indexes are a very important part of any reference source, particularly an extensive one, such as an abstract journal. Information is buried in extensive compilations unless keys are provided in the form of thorough and well-prepared indexes. There is considerable interest in the possibility of new kinds of indexes. Among these are (1) cipher indexes based on such new notations for chemical compounds as that worked up by G. M. Dyson and that by William J. Wiswesser; (2) citation indexes (a sort of genealogy of references) such as lawyers use; (3) chemical-group indexes, which might include ciphers; and (4) descriptor indexes, which provide selectivity of references by coincidence of terms. Coordinate or coincident indexes (based on the coincidence of terms) are coming into use.

Libraries. A discussion of chemical literature would be incomplete without mention of libraries. A number of the larger libraries in the United States specialize in scientific periodicals and books, and most of the University libraries are reasonably well stocked with such publications. A listing of the more important American libraries cannot be given here. A representative list of about three hundred American and Canadian libraries is to be found in the front of the List of Periodicals Abstracted by *Chemical Abstracts*, which List includes a key to library files.

In addition to doing a certain amount of inter-library lending many American libraries now have a photocopying service useful in widening the availability of their holdings. Some libraries also have a translating service.

Mechanization. The mountainous growth of scientific literature has stimulated interest in new and more facile ways of dealing with the problem of making this information available for use. During the past dozen years, efforts have increasingly been made to mechanize literature searching. Various punched card procedures have been proposed and some with certain limitations are in use. Efforts have also been made to bring modern electronics into the picture. Investigational work on literature mechanization, a worthy objective, continues.

No comprehensive mechanization system for a field as broad as the whole of chemistry and the related sciences in which chemistry is often used has been found as yet. The most important successful American project of this sort is that of the Chemical-Biological Coordination Center sponsored by the National Research Council, National Academy of Sciences. It is limited to chemical compounds (about 60,000 of them) with certain recorded biological properties correlated with coded structural elements. Dealing with the less definite information of broad fields is more difficult.

It can be said of literature mechanization that promising beginnings have been made in less comprehensive fields and with operation of the systems best kept in the hands of those who have built them.

Those working on mechanization are both limited and encouraged by the fact that (1) machines cannot think, but they can tirelessly do many things with great rapidity and accuracy; (2) machines cannot provide information which human beings have not, with forethought, put into them, but machines have real possibilities for the manipulation and helpful correlation of information; (3) machines cannot grow as can a human literature searcher during the course of a search, but there are ways to introduce opportunities for the latter kind of growth. One way is machine searching by steps, with the human searcher entering the picture between strides. At least the manipulation, correlation, and organization of information by machines may under some circumstances put information in a form more amenable to growth by individuals in the course of searches.

A good book on mechanization is "Punched Cards, Their Applications to Science and Industry", edited by Robert W. Casey and James W. Perry and published by Reinhold Publishing Corporation. (Second Edition, 1957).

E. J. CRANE

Cross-References: Documentation

CHEMICAL MICROSCOPY

In the chemical industry, physical as well as chemical properties are involved. Microscopy is especially helpful in answering physical questions in discovery, development, control, or service. Special *physical conditions* can usually be furnished under a microscope, such as special equipment for cooling or heating samples (cold and hot stage).

The observer works best when most relaxed and comfortable, according to three simple rules: (a) Always imagine that the object is far away (practically, at infinity); then the focussing muscles for the eye's lens are completely relaxed and their fatigue is at a minimum. (b) Keep the brightness of the image to a practical minimum (just slightly brighter than the conveniently lighted surroundings); then the iris diaphragm of the eye will not become abnormally closed and "microscope eye" and headache are avoided. (c) Keep both eyes open, even with a monocular, as continuous effort to keep the unused eye shut will tire the face muscles.

Magnification is "useful" when the finest detail is just visible to a person at a certain distance (10 in., unless stated otherwise). Any magnification over useful magnification is "empty magnification". Enlargement by projection of negatives of micrographs is sometimes "useful" especially in electron and x-ray microscopy.

In addition to pictorial images, microscopes may be made to produce descriptive and determinative patterns. Interference patterns by transmitted polarized light have long served to describe and

detect the architecture of *transparent* crystals, fibers, films and other oriented textures. Nowadays, optical figures produced by light reflected from opaque specimens are also being understood. *Electron* diffraction patterns in the electron microscope are useful, especially to identify thin layers without interference from their substrata. Microscopical absorption spectra in the visible or ultraviolet are obtainable by means of a "spectroscopic" ocular or camera. Infrared absorption microspectrometry has been made possible by the development of *mirror* objectives and condensers.

An identification may be performed microscopically by recognizing distinctive physical properties, or by making distinctive chemical derivatives. The latter are usually made by dissolving a "speck" of the unknown in a drop of solvent and reacting it with a reagent. The precipitated product is recognized by its crystalline habit or origin of color. Usually, the whole reaction is carried out dropwise on a microscope slide. Other times, the reaction is made in a capillary tube, single fiber or paper. If the unknown substance is mixed with other material (e.g. in ores and alloys) its *distribution* may sometimes be obtained by reacting the reagent on the matrix or its replica (chromographic contact printing). If the size of the unknown can be controlled or otherwise noted, the quantity of derivative may be roughly estimated or semi-quantitatively determined.

Physical properties are peculiar to physical chemical phases, rather than to strictly chemical composition. Therefore, physical properties differentiate among *polymorphic* phases (e.g. difference in hardness between diamond and graphite); and *pseudomorphic* phases (e.g. blue $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, vs. white $\text{CuSO}_4 \cdot \text{H}_2\text{O}$). Also, the fabrication and utility of substances depends largely on the physical properties of phase systems (e.g. the plasticity of putties, alloys, waxes, and formulated resins).

Determinative physical properties are many. There are those of *texture* (e.g. rocks, concretes); of "morphology" (e.g. starches, fibers, soaps, greases); "structure" (e.g. metals); and particulate "habit" (e.g. in emulsions, smokes, paints). There are *measurable* properties such as, length, area, volume, density, angles. *Microhardness* is measured for either descriptive or determinative purposes, on either a micro-indentation or a micro-scratch which was made under specified conditions. Microhardness differentiates one microscopic type of constituent or area from another.

There are *colors* with unpolarized light by absorption, reflection, refractive dispersion ("Christiansen" effect), selective particle sizes ("Tyndall colors"), structural (diffraction) colors. Polarizing the light allows the observation of birefringence (double refraction), pleochroism (oriented, specific colors by absorption or reflection). There are many other determinative *optical properties* including isotropy vs. anisotropy, one to three principal refractive indices and sometimes significant intermediates, optic sign (related to refractive indices but independently determinable), number of optic (isotropic) axes, the angle between two optic axes, orientation of optic axes, extinction angles.

There are determinative microscopical crystallographic properties. Crystal system and class are not directly observable but they are indicated by specific optical properties and crystallographic symmetry. There are various kinds of *faces*. Crystalline *habit* (sometimes loosely termed "form") is more indicative of conditions of crystallization than of crystalline architecture.

Kinds of Microscopes. There are many kinds and varieties of microscopes. Space will be taken to describe only three, especially important to the chemist: light stereomicroscope; a combination of "chemical" and "metallurgical" microscope; electron microscope. Common to all compound microscopes are the three essential optical parts ("optics"): *objective*, to form a real image of the object; *ocular* ("eyepiece") to magnify this image for the eye, camera, or viewing screen; and *condenser* (or vertical illuminator plus objective) for collecting the illuminating rays to a suitable spot on the object. There are many kinds and varieties of "optics".

For equipping the average chemical laboratory, the *stereoscopic microscope* (Fig. 1) is most probably the first light microscope to acquire. Being both *binocular* and *binoculative*, it is two microscopes, one for each eye. By obtaining simultaneously two slightly different views one gains some information about the third dimension of the object. The stereomicroscope also extends the visibility* of the eye beyond that of the "simple" microscope ("magnifying glass") and well into the range of the monobjective microscope. Among its advantages are an erect image and a relatively deep field in focus, so that manipulation of object and interpretation of image are natural and easy, even without experience; with such depth of focus, most specimens may be observed without preparation to render them flatter. Its chief limitations are relatively low visibility and crude illuminating systems, compared with monobjective microscopes.

The first microscopes used *transmitted* illumination and so were limited to "transparent" objects, such as biological and medical material; hence the name "biological" or "medical" microscope. Then mineralogists began using polarized light and a rotating, graduated stage to measure optical and crystallographic properties of transparent minerals in rocks; hence the name "petrographic". About 1900, Chamot took the best features of the biological and petrographic microscopes and designed the "chemical" microscope. Nowadays, there is little difference between the "petrographic" and "chemical" microscopes, and they are used interchangeably.

In modern chemistry and chemical industry, microscopes employing illumination reflected from the object are also important. Reflected or "vertical" illumination is achieved by bringing light in through the side of the microscope tube and, by means of a semi-transparent reflector, down to the

* Visibility is a combination of *resolution* and *contrast*. "Resolution" refers to the separation of parts of an object. By "contrast" is meant the distinction of the parts from their background.



FIG. 1. Binocular-Binoculative microscope with simultaneously rotatable polarizers.

object. Around 1864, Sorby used vertical illumination for studying metals, hence the modern terms, "metallurgical" microscope, "metallograph" (a photomicroscope) and "metallography". Around 1916, Murdoch studied the ore minerals microscopically by reflected light. They have distinctive color in polished section, by brightfield illumination or in dark-field illumination. Some of the anisotropic ore minerals show distinctive polarization colors between crossed polarizers of light. Polarizing microscopes employing reflected light are called "ore-microscopes". Second to the stereoscopic microscope, the chemist needs a *combination* of "chemical" and "ore" microscopes (Fig. 2).

Only some specialized microscopes may be mentioned in this space: grazing incidence ("ultra"), fluorescence, phase difference (and phase retardation) interference, image-converters ("snooper" or "sniper" scope; television; ultraviolet to color) "flying-spot" microscopes. Also to gain contrast there are special methods of illumination, especially various methods of "optical staining." There are special microscope stages such as mechanical, integrating (multiple mechanical) universal (3 perpendicular axes of rotation), cold, hot, furnace, schlieren cell, and electrophoresis cell. There are, too, many varieties of photomicrographic cameras.

With the *electron microscope* (Fig. 3) one has



FIG. 2. Combination of "petrographic" and "ore" microscopes.

unique visibility for at least three reasons: (1) by means of a stream of electrons of extremely short wavelength, he has a tool with at least 100 times the resolving power of the light microscope; (2) because the stream of electrons is scattered by a different kind of "density" than that which scatters light, he has another tool for gaining contrast; (3) because the angular aperture of the magnetic "lenses" is very small, depth of field in focus is at least 15 times greater than the depths at high powers of light microscopes.

The electron microscope has several limitations: (a) it and its accessories are expensive; (b) it operates in an extremely high degree of vacuum, presenting operating difficulties and affecting a specimen containing gases, liquids or certain solids; (c) the sharp focus of electrons may raise the temperature of the specimen to a destructive degree in a short time, reducing the period allowed for visual inspection and putting a burden on electron micrography. The expense can be reduced by purchase of a simpler electron microscope but then one is reduced to observation of materials requiring lesser visibility, but none the less important. Examples of such materials are pigments, fillers, catalysts, greases, latexes, films, fibrils and bacteria. Some of these may need to be "metalized" by vacuum deposition: at all angles to preserve them from the (b) vacuum or (c) heat of electron absorption; at one angle to give "shadows" and improved contrast.

In general microscopy or particularly in electron microscopy some materials may need special techniques of preparation: materials such as paint or clear films, molded or cast resins, glasses, ceramics and metals. Some of these techniques include

microtoming thin sectioning bulk materials or *replicating* unused, worn, accidental or experimental surfaces. Other materials require the highest powers of visibility of the electron microscope to reveal *either* the *functional* or the *fundamental* textures. Such materials include: viruses, phages, biological tissues, proteins, colloids and resins. By providing grazing incidence of the electron stream on the surface of a specimen, a *reflection electron image* may be obtained. This image is distorted but, properly interpreted, can be very informative.

A pencil of electrons from an electron condenser, incident on crystals produces a diffraction pattern which is similar to the x-ray diffraction pattern. The same determinative tables may be used. Because electrons do not penetrate far, reflection electron diffraction patterns have the advantage (over x-ray types) of representing *in situ* coatings, worn or deteriorating surfaces, surface phase changes, etc., without interference from their substrata. Transmission electron diffraction patterns are also manifested in the back aperture of the objective electron lens. Such patterns are distinguishable from those of associated crystals of a different phase.

X-ray microscopy may well become important to the chemist. To date, there is no commercially available x-ray microscope. But apparatus is



FIG. 3. Electron microscope, a commercially available type.

available for *microradiography*, the shadow resulting from a microspot of x-rays on the specimen in contact with a fine-grained, "photo-" sensitive film. Photographic enlargement of the x-ray shadowgraph is "useful" in that more detail is made visible to the eye 10 in. away, up to enlargements in the order of 100 or 200 diameters. While there are no compact lenses for focussing, x-ray microscopy, too, is being performed up to useful magnifications of the order of 200 diameters by linear projection of the x-rays, much like the pin-hole light camera.

There is a tilting specimen-holder for obtaining stereoscopic images with the conventional electron microscope. For observation at very high temperatures, the specimen is heated to emit its own electrons in the "hot emission" (Philips) microscope. For observing properties of crystals at extremely high resolution there is the "cold emission" (Mueller; Becker) microscope. Buerger produced "pictures" of molecules of phthalocyanine blue (and larger) by translating x-ray diffraction into a light image. Gabor and Bragg have worked on a microscope translating electron diffraction into a light image.

In chemistry, all microscopes are one kind of general tool rather than many specialized instruments. Their combined use is frequently necessary. In the solution of chemical problems, by microscopy, as by macroscopy, the functioning of the eye and brain are fundamental.

T. G. ROCHOW

Cross-references: *Optical Microscopy, Electron Microscopy, X-rays*

CHEMICAL NOMENCLATURE

General, Inorganic, and Organic, Including the Recommendations of the International Union of Pure and Applied Chemistry

The development of names for all that chemistry represents has been and still is one of its major concerns. It is obvious that every principle, fundamental concept, all elements, compounds and a multitude of other factors in the science must be labeled with a word or combination of words. To meet all these requisites there has been a constant attempt to make a coherent language of chemistry.

The word atom (Greek, uncut) is one of the oldest words of our present vocabulary and as far as ordinary chemical change is concerned (not counting nuclear fission) means about the same that it did when first used by Democritus c. 400 B.C. It is the least unit of matter involved in chemical reactions by means of which molecules or compounds are formed. The molecule is therefore a product made up of atoms of elements and represents a unit of matter able to exist alone and to exhibit a special set of properties of itself. The molecule is (except in the instance of certain gases) also a compound and as such has a chemical formula. This formula is so written to show the number of atoms of each element present. In other words, there are molecules of elements as well as molecules of compounds.

Each atom has what is known as a *symbol* made

of one or two letters, the first of which is always the initial letter of the name of the element, either in English or some other language, e.g. Se, selenium, W, Wolfram (tungsten). The weight ascribed to the atom is called the atomic weight (or symbol weight) and represents a chemically determined relation of its weight to that of oxygen = 16. The sum of the number of the symbol weights in a molecule of a compound is called a *molecular* or *formula* weight. An example: KNO_3 (potassium nitrate) = $\text{K} = 39.09 + \text{N} = 14 + (3 \times 16) = 101.09$.

The term *substance* is applied to matter which has a uniform or constant composition with one set of chemical properties. Accordingly, only *elements* and *compounds* can be strictly called substances. *Mixtures* and *solutions* may differ in that their composition can be variable and their properties would depend upon it. One of the most used terms in chemical nomenclature is *valence*—a word developed to describe the relative combining capacity of the elements as they form compounds. On a chemical basis the valence numbers are reckoned in terms of a value of 2 for oxygen or 1 for hydrogen. Hence, since in water 2 H atoms combine with 1 oxygen atom the valence of each H is 1, because it takes two atoms of this element to be chemically equal to 1 of oxygen. However, since the development of atomic structure the value of valence is usually given in terms of its valence electrons. The valence in respect to electrons is that number which represents the number of electrons gained or lost by an atom or a radical, or the number of shared pairs of electrons.

Inorganic Nomenclature

To demonstrate a naming system used in the chemistry of inorganic compounds it is necessary to introduce the words *ion* and *radical*. Ions in a general sense are electrically charged particles, and are usually capable of conducting electric current. Their main importance in chemistry relates to properties of solutions. A solution of an acid, base or salt has the property of electrical conductivity because of the presence in it of *ions*. They are either atoms of elements carrying an electric charge (e.g. H^+ hydrogen ion) or a number of atoms bound together in what is called a *radical* which is also charged, e.g. SO_4^{--} (sulfate radical). It is through these ions that acids, bases and salts have their existence as well as their properties.

A compound consisting of a H^+ (ion) in connection with a negatively charged radical, e.g. NO_3^- , is called an *acid*. In this case it would be nitric acid. The ions that carry positive charges are called cations (e.g. Cu^{++}) and those which are negative are called anions, (e.g. PO_4^{---}). A *base* is a compound made of a positively charged metal in conjunction with a negatively charged ion, called hydroxyl (OH^-). A typical case is K^+OH^- , potassium hydroxide. *Salts* are the product resulting from the combination of the positive ion of the base and the negative radical of the acid, e.g. K^+NO_3^- , named potassium nitrate. This general case, however, is not the only way salts can be formed.

The recommendations of the Committee of the

International Union of Chemistry on nomenclature are perhaps the best source of systematic naming of inorganic compounds which has been provided. [See *J. Am. Chem. Soc.*, 63, 889-897 (1941)]. There are still and probably will always be many names of chemical compounds that will be referred to with a colloquial term or expression that has little if any relation to any system. However, in the literature the only wise plan is to follow the recommendations of this committee for terms to use for inorganic and organic compounds. Even then many instances will arise that will present debatable problems.

Binary (two-element) compounds such as the common oxides, chlorides, sulfides, phosphides, etc. are usually named as follows:

MgO—magnesium oxide
KCl—potassium chloride
ZnS—zinc sulfide
Ca₃P₂—calcium phosphide

It is seen that the name of the most electropositive element is given first, and the name of the electronegative element is modified so that the last part of the name is changed to *ide*. Additional insight can be gained by a reference to:

HCl—hydrogen chloride
NaH—sodium hydride

The hydrogen changing from the first element to the last because of its relative electropositive nature in the first to a relative electronegative in the second.

In the naming of binary acids a special syllable is used to indicate the oxygen content:

HBr—hydrobromic
H₂S—hydrosulfuric
HCN—hydrocyanic

The names here are instructive, in relation to the system given below for oxygen-bearing acids. *Hydro* means "without oxygen". The name of the nonmetal is changed to give it a characteristic syllable—*ic*. In the cyanide radical the system holds.

The oxygen-containing substances have names for special reference to the oxidation state of the central element—the main element in the compound besides hydrogen and oxygen. In those compounds the suffixes *ic*, *ous*, *hypo*, and the prefix *per* are used. Sulfuric acid will serve as a full example.

H₂S—in aqueous solution—hydrosulfuric acid
H₂SO₃—in aqueous solution—sulfoxylic acid
H₂SO₄—in aqueous solution—sulfurous acid
H₂SO₄—in aqueous solution—sulfuric acid
H₂S₂O₈—in aqueous solution—persulfuric acid

The highest oxidation state of the element is given a name with *ic* as the characteristic syllable; one step lower is *ous*; the lowest oxidation state is indicated by the prefix *hypo*, which means "less than". There is no assurance that all these can be prepared in the free form.

While the above syllables are still in general use,

a strong recommendation is made that the Stock system should be used to indicate proportions by constitution. For example:

FeCl₂—iron (II) chloride—not *ferrous* chloride
FeCl₃—iron (III) chloride—not *ferric* chloride

The committee even goes so far as to say that the use of the older affixes should be discontinued in scientific literature. Some writers are already doing so. Compounds with an excess of oxygen are called *per* compounds, and there is usually a special way to account for the structure of compounds that can be so produced.

It should be observed at this point that the prefix *per* by no means tells the same thing about structure. For example, sodium persulfate is said to be a true *per* compound, but KClO₄, potassium perchlorate is not. This is a good example of how confusing words are still used in the nomenclature.

To continue the above system for acids as it is applied to salts, the following rules apply. The word acid is dropped, the name of the metal or radical is placed first, and the suffix syllables are changed: *ic* becomes *ate* and *ous* becomes *ite*.

Na₂S—sodium sulfide
Na₂SO₂—sodium (*hyposulfite*) sulfoxylate
Na₂SO₃—sodium sulfite
Na₂SO₄—sodium sulfate
Na₂S₂O₈—sodium persulfate

Sometimes it seems desirable to use other roots to aid in meaning, such as *mono*, *di*, *tri*, *tetra*, and *penta* from the classical languages.

CO—carbon *monoxide* (meaning one)
CO₂—carbon *dioxide*
AsCl₃—arsenic *trichloride*
CCl₄—carbon *tetrachloride*
P₂O₅—phosphorus *pentoxide*

Hydrates, as inorganic compounds, must be given special treatment, since they are common substances and at the same time more complex. Examples are copper sulfate, pentahydrate, CuSO₄·5H₂O, or sodium sulfate, decahydrate, Na₂SO₄·10H₂O. Convention is not uniform either in formulation or naming. Some writers use a comma between the anhydrous salt and water, which has been suggested, while others prefer a center dot, e.g., CaCl₂·6H₂O. Some name a compound of this sort calcium chloride, hexahydrate while others suggest calcium chloride, 6 hydrate. The first seems more prevalent and acceptable.

Hydrates involved above the introduction of another common term, viz., *anhydrous*. A substance usually a salt that can crystallize with water of hydration is called *anhydrous* when it is free of water. The same compound when united with a definite number of molecules of water is said to be hydrated or is a hydrate.

To show how difficult a perfect consistency is: the case of the above-mentioned sulfur compounds compared to those of chlorine should be examined. The chlorine oxygen acids are:

HClO—*hypochlorous* acid
HClO₂—*chlorous* acid

HClO_3 —chloric acid
 HClO_4 —perchloric acid

There should be a "hyposulfurous" acid, but it is recommended that the word sulfoxylic be retained.

Naming in respect to stoichiometric composition, the Greek numerical prefixes are recommended. These should precede, without hyphen, the constituent which they represent. This plan is applied chiefly to nonpolar compounds. For prefixes above 12, Arabic figures are used for simplicity. Examples are:

N_2O_3 —dinitrogen trioxide
 N_2O_4 —dinitrogen tetroxide
 $\text{Fe}(\text{CO})_4$ —iron tetracarbonyl

Intermetallic Compounds. No rigid system of naming is recommended for this class of compounds. The best usage is formulation, in which the exact distribution by atoms is shown. Example: $\text{Cu}_3\text{Sn} \cdot \text{Cu}_3\text{Al}$. Designation of atomic number, atomic weight, and state of ionization is as follows:



These are read as follows:

Upper left atomic weight or mass
 Lower left atomic number
 Upper right state of oxidation
 Lower right number of atoms per molecule

Naming within groups of elements: While the term halide for the halogens is widely used, it is strongly urged that *halogenides* replace it.

Names like alkali elements and alkaline earths should be discontinued, but it is good form to retain "alkali chloride".

The prefixes *ortho*, *meta* and *pyro* are used in relation to the degree of hydration which an anhydride can undergo to form an acid or a salt: Anhydride

$\text{P}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HPO}_3$ —*meta*-phosphoric acid
 $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4$ —*ortho*-phosphoric acid
 $\text{P}_2\text{O}_5 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{P}_2\text{O}_7$ —*pyro*-phosphoric acid

The accepted meanings are: *Ortho*, fullest possible hydration; *pyro* (Greek, fire) made from *ortho* by use of heat; and *meta*, lowest stage of hydration.

Salts containing hydrogen: The I.U.C. committee urges a change in the name for hydrogen-bearing salts to a system different from much of the common practice in current writing. Such compounds as NaHCO_3 are to be *sodium hydrogen carbonate*, not sodium bicarbonate. KHSO_4 is potassium hydrogen sulfate; Na_2HPO_4 is orthodisodium hydrogen phosphate. Salts containing a hydroxyl radical are to be called hydroxy compounds; $\text{Ca}(\text{OH})\text{Cl}$, would be called calcium *hydroxy* chloride.

Complex Compounds. The system devised by A. Werner is to be followed as far as possible. Use is made in this plan for a letter to be used in place of a Roman numeral to indicate the valence of the

central element. For example:

I = a
 III = i K_2PtCl_6 = Potassium hexachloroplateate
 IV = e

There seems to be a growing use of the Stock system of naming rather than that based on the Werner plan. This may be due in part to the lack of euphony in the words. Stock suggested the use of Roman numerals in parentheses after the name of the central element to refer to its oxidation state:

FeCl_3 would be iron(III) chloride
 FeCl_2 would be iron(II) chloride

In the case of anions:

KMnO_4 potassium permanganate (VII)
 K_2ReCl_6 —potassium (hexa) chlororhenate (IV)

Coordination compounds can also be fitted into the Stock scheme easily and systematically. Examples:

$\text{K}_4[\text{Fe}(\text{CN})_6]$ Potassium hexacyanoferrate (II)
 $\text{K}_3[\text{Fe}(\text{CN})_6]$ Potassium hexacyanoferrate (III)
 $\text{K}[\text{Au}(\text{OH})_4]$ Potassium tetrahydroxoaurate (III)

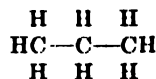
In regard to the recommended plan for naming isopoly, heteropoly, double salt compounds, hydrates, the use of hyphenation for hydrates and the ammoniates, see *J. Am. Chem. Soc.*, **63**, 895–897 (1941).

Organic Nomenclature

There are three essential facts with which to deal in the nomenclature of organic compounds: (1) The common names of long and accepted usage; (2) the Geneva System, dating from the Congress held in 1892; (3) the report of the Commission on Reform of Nomenclature in Organic Chemistry. This study was in 1930 in Paris. The reference in English to the 68 recommendations is in *J. Am. Chem. Soc.*, **55**, 3905 (1933).

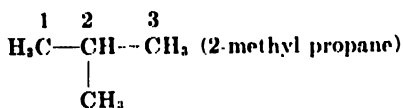
The Geneva System is based on compounds derived from hydrocarbon as a starting point, and the names correspond to the longest straight carbon chain which is present. The position is usually indicated by numbers applied to the carbons of the straight chain. The numbering beginning with the end carbon nearest the substituent element or group.

The *normal* compound is one in which the carbons are linked one to another in a straight chain. These are named such as ethane, propane, or pentane. Normal propane would be:

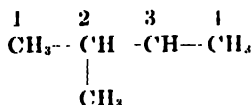


It is necessary therefore to consider only the

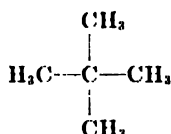
branched compounds, e.g.:



To put the idea another way, it is a derivative of propane, not of methane. A certain pentane, for example, was once known as isopentane. Its structure is:

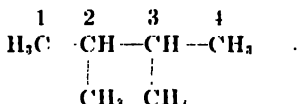


It is now named in accordance with the system 2-methyl butane. The 4 carbons in a straight line give rise to the name butane and the side group is attached the *second* carbon atom in the chain. Another pentane has the structure



and was once named tetramethyl pentane. Under the Geneva System it is named in terms of 2 methyl groups being joined to carbon number 2 in a propane chain. It is thus 2,2-dimethyl propane.

An example from the hexanes ($\text{C}_{12}\text{H}_{14}$) can be studied as follows. It could be called (old name) tetramethyl ethane:



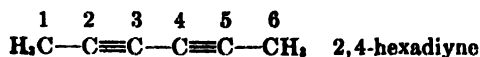
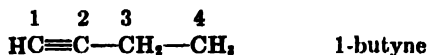
Its name is actually 2,3-dimethyl butane.

Some special recommendations which follow and extend the Geneva System defines the use of certain syllables.

Open-chain hydrocarbons with one double bond should end in *-ene*.

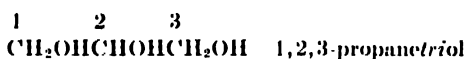
Open-chain hydrocarbons with two double bonds should end in *-diene*.

Their names would now be alkenes, and alkenes. Triple bond compounds end in *-yne* and *-diyne*. It is important to note that propyne is a change from the Geneva System, which would call the same compound called propyne. It is suggested that acetylene will probably never become ethyne, but to illustrate the application and practice applied to higher hydrocarbons these examples will be instructive:



Aromatic hydrocarbons should end in *-ene*, e.g., "phene" might be used in place of benzene.

Alcohols are to be named by use of the hydrocarbon name with *-ol* as the characterizing syllable: phenol, from phene, and naphthol, from naphthalene. In order to extend this plan to polyhydric alcohols, a syllable such as *di*, *tri*, and *tetra* will be inserted between the name of the parent hydrocarbon and the suffix *ol*.



The name *mercaptan* is to be discontinued and thiol used in its place. $\text{C}_6\text{H}_5\text{SH}$ is benzenethiol.

Sulfides, disulfides, sulfoxides and sulfones will be named like ethers, the oxy- term being replaced with thio-, dithio-, sulfinyl and sulfonyl.

The acids are also named in accordance with the Geneva System. For a detailed discussion of the naming of acids the report on which this article is based should be consulted.

F. A. GRIFFITHS

Cross-references: *Chemical Terminology, Formulas, Atoms, Molecules, Acids, Bases*

CHEMICAL RESEARCH

A continuing steady growth of chemical technology requires a proper balance between fundamental and applied research. The phenomenal growth of the industry during recent decades is certainly dramatic proof of the vitality of applied research during this period. A sustained growth in future decades will prove that our present fundamental research effort also is adequate.

There is a growing awareness on the part of industry that the twentieth century economy was born with a valuable inheritance of well developed scientific understanding. In the field of chemistry proper, that is, molecular architecture, the basic laws of chemical reactions were quite well understood in terms of atoms and valence. Thermodynamics, the science which provides such powerful quantitative generalizations of myriads of chemical observations, had been completely developed. Classical physics had also reached a stage of considerable maturity, although its important contributions to chemistry by way of quantum theory and wave mechanics were to come during the first quarter of the twentieth century. Industrial research as we know it today did not exist, indeed, had not even been conceived. The word "research" needed no qualifying adjective such as "basic" or "fundamental", "developmental" or "applied" and "product", in order to explain what kind of research was meant. There was essentially only one kind of research, and this was what we now refer to as "pure" or "basic" or "fundamental".

The birth of modern industrial research, which is more inclined to applications, had necessarily to wait for pure research to reach a certain stage of maturity. It is being recognized, however, that the legacy of scientific understanding must constantly

be extended if continued success in application research is to be expected.

Fundamental research is essentially a matter of inquiring into nature. The motivation for this activity is only imperfectly understood, but it is primarily an intellectual pursuit. Unlike applied research, the reward being sought is attained through the ability to understand and explain natural phenomena. The interest centers on elucidating the laws of nature, not on manipulating or exploiting them. Perhaps for this reason fundamental research has sometimes been referred to as "pure", presumably because of an emotional attitude on the part of those who use the term that is opposed to exploitive activity.

Liebig has been credited with the statement that, "To one man science is a sacred goddess to whose service he is happy to devote his life; to another she is a cow who provides him with butter." Value judgments of this kind are usually rejected as intellectual snobbery by present-day scientists, both fundamental and applied. Nevertheless, the fact remains that the interests and motivations of those engaged in research vary enormously, and that these temperament factors more than anything else determine whether an individual will center his interest in fundamental or applied research. In order to maintain an adequate supply of fundamental research scientists, it is necessary for society as a whole to appreciate and affirm the spirit of scientific investigation for its own sake.

Prior to World War II the chemical industry in the U.S. had already begun to recognize the necessity of making its own contributions to basic research rather than relying entirely upon the academic institutions, as had been done during the early part of the century. Du Pont, for example, pioneered in the chemistry of elastomers and polymers and quickly utilized the new learning to develop such products as neoprene and nylon. Characteristically, the relatively small amount of really new learning thus acquired opened up a possibility for new applications of such magnitude that it has supported many years of intensive exploitation in the form of applied research. The significance of the words of Goethe, "He who advances science may say to himself that he is laying the groundwork for unlimited results to come" becomes clear in the present age.

With the outbreak of the second world war and the interruption of German scientific contributions, the U. S. government very wisely recognized the need for large-scale sponsorship of scientific research. Naturally, much of the sponsored work was "applied", in the sense that it was directed either toward new weapons or products required by the wartime economy. Nevertheless, much fundamental work was also done, and for the first time in history the center of basic scientific investigation shifted from Europe to America. Many of the dramatic wartime developments were founded upon basic European discoveries, such as penicillin, DDT, polyethylene and the synthetic detergents. On the other hand, some of the synthetic rubbers and the whole of the complicated

body of chemistry associated with the atomic energy development were almost entirely American.

It has often been said, on both sides of the Atlantic, that although the United States is the recognized leader in applied research, most of the fundamental research is contributed by European laboratories. This was undoubtedly true during the first half of the century, but there is some reason for believing that it is no longer so. While the question is a very difficult one to treat quantitatively, it may be reasonable to assume that the ratio of American to European Nobel Prize winners in physics and chemistry is a fair index of basic research activity. The percentage of Nobel Prizes in chemistry and physics awarded to Americans rose from 4.2% during the first decade to 9.1% during the third decade, and in the interval 1940-1950 mounted to 36.8%. This does not mean, however, that the ratio of basic to applied research has undergone any such change within the United States, but perhaps only that the total research activity has increased at a much greater rate than in Europe.

Another effect of the war was that a whole new methodology of research had to be developed because of the necessity for haste. It was no longer feasible to depend upon the success of individual investigators; instead, teams were encouraged to attack specific problems with definite objectives for each member of the team. This new, highly organized research method has been spectacularly successful in many cases, but probably not as economical of men and money as the more leisurely accomplishments of individuals. To some extent, the pattern developed by the government during the war is similar to the industrial research method which was already in the formative stage, but on a much larger scale. The justification for it in a peacetime economy, for anything other than problems very close to application, may be questionable.

At the conclusion of the second world war the contributions of scientific research had been so spectacular and had achieved such wide public recognition that the Federal government adopted a policy of continuing support on a broad basis. The Office of Naval Research was conspicuous among government agencies in the support of basic research, even though it might be entirely lacking in any foreseeable application. The Atomic Energy Commission has also continued sponsorship of fundamental work, though in general the subject matter of the sponsored work has had a relation to matters of special interest to the A.E.C. Many of the other government agencies have also sponsored research, both chemical and physical, but in general it has been directed to specific problems. In the past few years, since the birth of the National Science Foundation, the ONR and other government agencies have been gradually withdrawing support of the more basic research and the National Science Foundation has in many cases been assuming these responsibilities. It is to be hoped that this far-sighted policy will be maintained and strengthened in the

future. Sponsorship of only applied research by the government agencies tends to drain off talent from the basic science fields and may, in the long run, constitute a serious disservice to the nation.

Basic research in chemistry very often crosses over into fields variously known as physical chemistry, chemical physics or molecular physics. Thus, chemistry, the science, is in reality the physics of the extra-nuclear electrons of atoms and molecules. The elucidation of the Periodic Table of the elements with its many irregularities, the understanding of the various kinds of chemical bonds, and in fact all the nonempirical generalizations of chemistry owe their existence to the atomic theory of Rutherford and Bohr. On the other hand, the earliest and, in many respects, most convincing evidence for the existence of atoms was provided by chemistry rather than physics. The empirical laws of definite proportions and multiple proportions led directly to the concept of atoms. It is also true that the whole elaboration of structural chemistry occurred with relatively little aid from physics. Physics has not progressed sufficiently to be able to deal in any exact way with the complex molecular structures which are the everyday problems of organic chemists. Even in this field, however, the physical concepts derived from wave mechanics such as "resonance stabilization" and "hydrogen bond" are of great use to the chemist. Thus basic chemistry as a science merges with physics. Only in the application of the science is there a complete divergence in the subject matter.

Applied research has brought about astonishing changes in almost all fields of human activity during this century, and while it is impossible to separate out the importance of the contributions of the various sciences, chemistry has certainly accounted for a large part of the evolution. Agricultural productivity, for example, has been multiplied enormously, partly because of the development of new machines, but also because of the availability of chemical fertilizers, insecticides, soil conditioners and plant growth regulators of various kinds which were unavailable and even unknown fifty years ago. Medicine has been assisted immeasurably by the many pharmaceutical preparations, the antibiotics, vitamins and hormones. These developments are in large part responsible for increasing the life expectancy from 48 years in 1900 to 68 years, which is the present figure for Americans. At the same time, the cost of these precious substances has been constantly decreased by improved manufacturing processes.

The textile industry has experienced a virtual revolution because of the introduction of many new synthetic fibers, most of which have come within the last twenty-five years. At present the quantity of chemical fiber consumed in the United States, including viscose rayon, is twice as great as the amount of sheep's wool. Perhaps equally important is the fact that entirely new properties are to be had in the synthetics which permit the development of new products and substantial improvements in old ones. Produced as continuous sheet rather than fiber, many of the polymers are making revolutionary changes in

methods of packaging and distributing food products and other materials. These changes, together with the enormous improvements in transportation, have made it possible for the United States to surpass all other nations in the quality and selection of foods available everywhere in the country regardless of local climate or season. The polymers have, of course, made enormous contributions to the fields of protective finishes and as paints and varnishes, floor coverings, molded parts for appliances, automobiles and homes, and virtually every other industry.

Simultaneous advances in the chemistry of dyes and pigments have kept pace with the textile and molded plastic revolution so that our products are not only cheaper, but are also brighter and more colorful than ever before. Color in the graphic arts has reached a peak of perfection undreamed of in 1900, and even the amateur photographer may enjoy the remarkable achievements of the color chemists.

The profusion of new products is much too great to be enumerated, even by categories. Petroleum chemistry, as well as bringing us our modern fuels and lubricants, has made possible many of the excellent synthetic detergents, plastics and a host of other products. Silicone chemistry, still in its infancy, has already yielded improved waterproofing agents, electrical insulation materials, high temperature stable elastomers, as well as better waxes and finishes. New advances in extractive and process metallurgy have made available as industrial materials metals which were only laboratory curiosities a few years ago. The rapid proliferation of new materials is exemplified by the fact that over 50% of the present products of the du Pont Company have been developed within the last twenty-five years.

Even though great progress has been made in basic chemical research to date, there are still vast fields of chemistry for which little or no detailed understanding exists. Undoubtedly chemists of the future will not be content with the present state of knowledge in these areas. Virtually all organic chemical reactions proceed through the medium of free radicals and similar fragmentary molecules. Many of these substances have been detected spectroscopically and also chemically, and in some cases certain properties can be inferred, but in general very little is known of them. Catalysis, combustion, polymerization and all high-temperature reforming reactions must remain empirical until a better understanding is formed of free radicals and reaction mechanisms.

Ever since the synthesis of urea by Wöhler in 1828 the fundamental distinction between "vital force" and "inert" chemicals has been constantly receding. And yet the synthesis of life itself, even the lowly life of a virus, continues to elude the chemist. Careful and ingenious investigations have elucidated certain portions of metabolic chemistry of remarkable complexity, but the chemistry of self-duplication is still unknown. Closely related to this is the chemistry of immunology, enzymology and heredity.

The rapidly growing list of chemical elements which are becoming available as industrial mate-

rials will certainly attract the attention of applied research chemists. Organic compounds, including polymers, containing metals such as titanium, zirconium, molybdenum and tungsten, to mention only a few, show promise of providing new and interesting products. The combinations are almost inexhaustible. So long as a proper balance is maintained between basic and applied research it would appear that we need never fear a scarcity of new developments, the life-blood of an ever expanding technology.

HOWARD O. McMAHON

CHEMICAL TERMINOLOGY

Modern chemical terminology is a complex pattern, the resultant of three major influences and several lesser factors. The primeval influence is the age-old human habit of naming things from ready-to-hand materials, or from some appeal to one of the five senses, or from primitive civilization's four elements (earth, air, fire, water), etc. Next in time comes the even more haphazard practice of introducing words into terminology, especially in the process industries, which accumulate into the "jargon" of the industry. Latest in time, and the only systematized major influence, is standardization of nomenclature, symbols and abbreviations by committees and commissions.

Among the tributary factors are the introduction of proper names (usually of discoverers or places) into the language; the tradition that discoverers (especially of elements) are entitled to name the discovery; and unabashed borrowing of terms from foreign languages (probably English now contributes more than it takes).

Just as primitive man used stones, wood, animal hides, bones, and fire to make what he needed, so the alchemists used whatever was handy in their experiments. Thus we have many chemical names with nearly forgotten origins, rooted in Latin, Greek or Arabic names of common products. Often the chemical has no apparent resemblance to the parent product; thus, formaldehyde is not reminiscent of *formica* (ant) (though formic acid is), and chloroform has almost lost the connection. Other common stems are acet- (*acetum*, vinegar); amyl (*amylum*, starch); vinyl (*vinum*, wine); but- (*butyrum*, butter); lact- (*lactus*, of milk); sacchar- (Arabic *sukkar*, Latin *saccharum*, sugar); oleo- (*oleum*, oil); lipo- (*lipos*, fat).

Responses to the senses contribute many stems, e.g. glyc- (*glykos*, sweet); oxy- (*oxys*, sour); acryl, acrol- (*acer*, sharp and *olere*, smell); (e)muls- (*mulsus*, soft); aur- (*aura*, glow, and *aurum*, gold); phon- (*phone*, sound). Color has been especially prolific, e.g. with leuco- (*leukos*, white); melan- (*melanos*, black); chrys- (*chryseos*, golden); erythro- (*erythros*, red); chlor- (*chloros*, green); cyano- (*kyanos*, blue); porph- (*porphyros*, purple).

The most recent of the major influences, standardization of nomenclature, terminology, symbols and abbreviations by agreement, has single-industry, single-society, national and international facets. Trade associations and scientific societies have their committees (ACS and its

divisions have several); the standards associations (American Society for Testing Materials, American Standards Association, International Standards Association, and numerous national societies) all participate; and the International Union of Pure and Applied Chemistry (IUPAC) is particularly active in working for better nomenclature.

These efforts are not new; rapid developments in discovery and synthesis of new compounds in the middle and late 1800's led to tremendous confusion, and earnest efforts at agreement among chemists. In 1892 these efforts culminated in the Geneva Congress, where the base of nomenclature now known as the *Genera System* was proposed. This was ultimately hammered into the form which is still the foundation of IUPAC nomenclature although there are now many differences in detail.

The traditional right of discoverers to name elements has been largely responsible for the several instances of two or more names persisting (sometimes until settled by international agreement) for the same element. Examples are Cb-Nb, Gl-Be, Il-Pm, Cp-La, Ct-Hf, Ab-At, Ma-Tc, AeK-Vi-Fr, Em-Nt-Rn.

Borrowing from foreign languages is an old game with lines crisscrossing in all directions. As a few of many acquisitions in English we have *caoutchouc* from Tupi via French; *bismuth*, *cobalt*, *nickel* and *zinc* from German; *camouflage* from French; *alcohol* and *alkali* from Arabic; *whisky* from Celtic; *kuolin* and *ginseng* from Chinese; *brandy* and *pickle* from Dutch; *granite*, *lava* and *stucco* from Italian; *gingko*, *sake* and *soy* from Japanese; *cider* from Hebrew; *guttapercha* and *sago* from Malay; *borax*, *lemon*, *lime*, *orange*, *musk*, *pistachio* and *rice* from Persian; *marmalade* and *molasses* from Portuguese; *chernozem* and *podzol* from Russian; *chaulmoogra* and *khaki* from Sanscrit; *slag*, *tungsten*, *flake* and *egg* from Scandinavian; *cork* and *sherry* from Spanish; and as a prize example, remacadamizing from *re* (Latin), *mac* (Celtic), *Adam* (Hebrew), *iz* (Greek), and *ing* (Anglo-Saxon).

Symbols, chiefly chemical and mathematical, and abbreviations are extremely important factors in chemical terminology. Symbols have had many origins, often whimsical, and often one concept has had several symbols, or one symbol served for several concepts. Some of these overlaps have been clarified by agreements, often international; some survive to this day. Abbreviations, though supposedly based directly on the parent terms, sometimes take peculiar forms. This is especially true in shifts from language to language, as in lb. for *pound* and oz. for *ounce*. Agreements have not yet eliminated all the confusion between g. and gr. for *gram* and *grain*. But progress has been made and the situation continues to improve.

Along with the symbols and abbreviations go the chemical notation systems, which combine both. Among the pioneers in this field is Dyson with his system for organic compounds. A committee was appointed by ACS to cooperate with IUPAC in comparative studies looking to adoption of a single system, and the National Research Council in Washington also made a survey of

systems. None has been officially approved by IUPAC (1956).

Literature. Foremost among the reference works used in preparing this discussion is Roland Wilbur Brown's "Composition of Scientific Words" (published by the author, U. S. National Museum, Washington, 1954). Others to which readers are referred for more detailed information are the following, selected partly for direct reference and partly as guides to the voluminous literature:

A. General terminology.

1. Hackh's Chemical Dictionary, Ed. 3 (revised by Julius Grant), Blakiston, New York, 1953.
2. Condensed Chemical Dictionary, Francis M. Turner, editor; Ed. 5, (revised by Arthur and Elizabeth Rose), Reinhold, New York, 1956.
3. Webster's New International Dictionary, Ed. 2, G. and C. Merriam, Springfield, Mass.
4. Dictionaries and Grammars in 125 Languages Including Scientific and Technical Dictionaries, Stechert-Hafner, New York, 1955.

B. Chemical nomenclature.

1. Naming and Indexing of Chemical Compounds by *Chemical Abstracts*. (Introduction to the 1945 Subject Index). Issued by *Chemical Abstracts*, Columbus, Ohio, 1946.
2. E. J. Crane, Standardization of Chemical Nomenclature (reprint, 1931, available from *Chemical Abstracts*; bibliography to 1931).
3. Rules for Naming Inorganic Compounds (International Union Report for 1940), available from *Chemical Abstracts*.

C. Notation systems.

1. G. Malcolm Dyson, New Notation and Enumeration System for Organic Compounds, Ed. 2, Longmans, Green, New York, 1949.
2. Which Notation? (review), *Chem. Eng. News*, 33, 2838-43 (1955).

JULIAN F. SMITH

Cross-references: *Chemical Nomenclature*

CHEMICAL TESTING

Basically, the science of chemistry depends upon the testing and analysis of materials. What is a material? Is it suitable for some specific purpose? Can it be made in a different form? Or can other materials be made from it? These and many other questions can only be answered after one or many chemical tests. There is essentially no difference between the work of analysis done in the chemical laboratory of a university and that done in a commercial testing or an industrial laboratory. Perhaps the work of the latter is geared to economic cost rather more than university work, though this distinction is not clear cut and cannot always be made.

Very broadly, most analysis can be classified as (a) specification and control; (b) general and miscellaneous; (c) research.

Specification and Control. Does a product meet certain requirements? Are all things present in the correct proportion? Specific tests must be made to find out and so control the manufacturing process. The tests employed are usually streamlined to produce just the desired result with no more and no less than the necessary accuracy. Any method that will quickly and cheaply give this answer may be used. Industries have united to back organizations that publish specifications and methods of test used by these industries. The American Society for Testing Materials (A.S.T.M.) is an outstanding example of this concerted effort. Among other standard methods are those published by the Association of Official Agricultural Chemists (A.O.A.C.), the American Oil Chemists Society (A.O.C.S.), the American Petroleum Institute (A.P.I.), the Technical Association of the Pulp and Paper Industry (T.A.P.P.I.). The United States Pharmacopoeia (U.S.P.), the National Formulary (N.F.) and Federal Specifications also publish standard tests.

General and Miscellaneous. A large part of the work carried out in the analytical laboratories of a commercial testing firm or of an industry comes under this category. It answers such questions as, Is a competitor's product as good as ours? What is wrong with this material? Does this reaction show promise? Has what we set out to do really taken place? All answers to such inquiries are solved in these laboratories.

Research. This embraces a wide field. New products are dependent on chemical analysis for their existence, especially so in these days of rapidly multiplying new drugs, new types of metals for automotive products and anti-corrosive use, materials for building and the many products that are raising our standard of living. All are based on research backed up by analysis. Special laboratories are often set apart for research in methods of analysis. This work may not always show immediate results in terms of economical operation, but will almost invariably do so in the long run. Laboratories of a national character such as the Mellon Institute of Industrial Research in Pittsburgh, Pa., have been established for fundamental research in basic industries.

Methods of Analysis. These can be divided into two categories: (1) Classical or wet methods and (2) Instrumental methods.

Classical methods. Depending upon the specific chemical properties of the elements and their compounds, a large body of methods have been proposed and refined after much study until specific tests and determinations are made, using traditional "beaker and solution" methods, for specific purposes. These methods are, in general, of utmost value and will not readily be replaced. They are the methods upon which all chemical analyses are based and to which they are referred. Analyses made using macromethods usually comprise the majority of determinations. Micro-methods in which special technic and apparatus

are employed, and spot tests, whereby very small quantities of substances normally in solution are reacted to give specific results also find much use. A combination of these three types of methods may be used in one analysis.

Instrumental methods. Sometimes an instrumental method alone will give the desired information: an oil may be identified with infrared equipment. On the other hand, in many cases these methods are part of a normal chemical analysis and must include much chemical preparation and final chemical interpretation. Using equipment that can detect and measure significant physical phenomena, generally x-rays, ultraviolet, visible and infrared rays, much data can be obtained that would not be available otherwise. Electrical behavior of solutions is made to produce useful qualitative and quantitative data. Radiochemical methods are included in this category. They depend largely upon spontaneous emission of rays—usually gamma rays from radioactive materials and isotopes.

This branch of analysis has recently grown rapidly, keeping pace with the ability of manufacturers to produce more sensitive instruments for detecting all types of radiation and electrical phenomena. It is important to note that such instruments are calibrated against accurate classical "wet" analysis.

Typical Analytical Procedure. Sampling. The most meticulous analysis is of no use if a proper sample is not used. This first step is of the utmost importance. Methods of sampling vary with gases, liquids, and solids. Standard methods of sampling are often available, e.g., the A.S.T.M. method for sampling coal.

Preliminary examination. If the sample composition is unknown, well directed qualitative tests will save much subsequent work. Appearance, odor as is and on heating, flame tests for characteristic color indicating certain metallic elements, acidity or alkalinity using a pH meter or universal indicators, liquid or paper; effect of acidification (a gas may be evolved, with or without an odor), quick spot tests and tests for anions—all can usually be performed in a relatively short time and will normally characterize the substance.

Choice of method. Assuming the general composition to be known, the best method of analysis must then be thought out. In many cases, a number of determinations may be made on one sample after appropriate preparation. A careful choice in the use of methods must be employed.

Interpretation and Presentation of Results. Results should be expressed only to the desired significance and should not be made to appear more accurate than they are. Very small amounts are normally expressed as parts per million (ppm). When gases or liquids are analyzed it is necessary to definitely express results as by weight or by volume. Good work necessitates good mathematical interpretation. Particularly in repetitive analysis when many samples are dealt with, the use of statistical methods can both indicate the precision of the analytical method and also the

minimum number of samples it will be necessary to analyze from a batch to know whether or not the whole batch falls within set specifications.

FRANKO M. BIFFEN

Cross-references: *Analytical Chemistry; Exposure Testing*

CHEMICAL WARFARE

Chemical warfare is the term used to describe the direct action of chemicals as weapons. The chemical is used not as an explosive to propel projectiles, but to cause casualties itself directly by irritation, burning, asphyxiation or poisoning, to contaminate ground, to screen or to decrease an enemy's fire power by smoke, and to damage by incendiary effect.

Most chemical combat substances are liquids or solids. Some are fired in shells or bombs which explode and disperse the chemical in drops or as aerosols. Some are vaporized by heat within a container. Others are carried in tanks on airplanes and released to fall as a spray or dust. A few that are very volatile can be released directly from pressure cylinders to form a cloud carried by the wind.

For every offense there is a countermeasure. Within a few days after the first attack with chlorine by the Germans (April 22, 1915) troops were issued gauze pads and soda solution to hold over mouth and nose. Next came cloth helmets impregnated with chemicals to neutralize chlorine and phosgene. Then came box respirators with tight-fitting face masks attached to canisters of absorbents by tubes or directly. Today the principal adsorbent is activated, impregnated charcoal. The arsenical smokes caused addition of a mechanical filter. At first this was a layer of towelling; later felt was used, and then special cellulose filters were developed which surround the container in which the adsorbent is carried. When mustard gas was introduced it became necessary to dress the soldier in impermeable clothing and boots. Following World War I the United States Army developed a compound called impregnate which makes cloth safe against mustard vapor. In World War II a uniform impregnated with this chemical was available for each soldier in case of gas warfare.

Research in chemical warfare continues. Today the *nerve gases* appear to hold first importance. Although atomic weapons have diverted the public from much thought about gas warfare, the threat of chemical attack in any future war is great. Large scale gas attack on cities has never been attempted. The fact that it is effective, very much cheaper than atomic attack and can be accomplished without destruction of the target may lead an enemy to use gas instead of atomic explosives. The existence of such effective agents makes surprise attack on civil populations a very serious threat.

Biological warfare is defined as the intentional use of living organisms or their toxins to injure man, animals or crops. It is considered practicable and constitutes a definite threat in war. As a re-

sult of preliminary studies and intelligence reports the U. S. Chemical Warfare Service was directed in November, 1942, to conduct necessary research and formulate defensive and offensive measures. Small amounts of agent may cause great damage. It can be developed and produced in small laboratories and plants so that its production would be difficult to detect. Most scientists agree that epidemics cannot be created intentionally. Biological warfare does not require that an agent be able to create an epidemic to be useful as a weapon. The number of biological agents that may be useful in war is not large. Research efforts are directed toward protective measures and methods of disseminating fragile and delicate biological materials. The United States is not unprepared to cope with an attack of this nature. Biological warfare has never been used by the United States.

It has been recognized that radiation may be used as a weapon aside from its connection with the atomic explosion. Radioactive materials obtained in the production of fissionable products might be disseminated deliberately as clouds or dusts to cause casualties. This could be done without causing destruction of buildings and industrial plants.

Classification of Agents. The three main groups of chemical agents are gases, smokes, and incendiaries. A war gas is defined as a toxic or irritating chemical used for its effect on personnel. A screening smoke is one used to deny observation or reduce effectiveness of aimed fire. A signaling smoke, generally colored, is used to convey a message. An incendiary is used to ignite combustible material or cause casualties. The normal physical state of an agent determines to some extent its tactical use, persistency, physiological action and type of munition in which it may be used.

The concentration of an agent is the amount present in a unit volume of air at the target, generally expressed in milligrams per cubic meter. Agents are classified as to physical state, tactical use, physiological action and persistency.

According to tactical use a war gas may be a casualty or a harassing agent. A casualty gas has such characteristics that a dangerous concentration can be set up on the battle field. A harassing gas on the other hand is one like a tear gas which in very small concentration will force masking and slow operations. The tactical classification also includes smokes and incendiaries.

Gases. The war gases are divided as to physiological effect into six classes: (1) the choking gases, which attack the respiratory tract; (2) the blister gases which inflame and cause general destruction of tissue of body surface and interior; (3) the blood gases which, when absorbed into the body by breathing, swallowing or through the skin, affect body functions by their action on the blood; (4) the nerve gases, absorbed in the same ways, affect by their action on nerve structure; (5) vomiting gases cause nausea, sneezing, and intense pain in head; (6) the tear gases (lachrymators).

If the concentration of an agent remaining on a target is sufficient after ten minutes to require protection of any kind the substance is termed

persistent. A moderately persistent agent is effective from ten minutes to 12 hours and a highly persistent more than 12 hours. An agent effective for less than ten minutes is nonpersistent.

There are ten requirements for a theoretically ideal war gas. It must be: (1) effective in low concentrations; (2) unreactive, and so not easily destroyed; (3) easily manufactured in large quantities; (4) composed of easily procurable raw materials; (5) cheap; (6) easy to transport; (7) stable on storage and against shock of explosion; (8) heavier than air; (9) effective against all parts of the body; (10) not easily detected. Every war gas should combine the first five attributes.

A choking gas must be so volatile or easily dispersed that an effective concentration may be produced before a man can mask and so powerful that one or two breaths will cause a casualty. The typical choking gas is phosgene (CO), carbonyl chloride. When breathed in low concentrations it may not be immediately irritating. It is cumulative in its effects. Symptoms are coughing and choking, then hurried shallow breathing and sometimes vomiting, followed by severe chest pain and cyanosis, with red bloated face, or with grayish pallor indicating failing circulation. Sometimes there is a delay of several hours before effects are felt.

Pure phosgene is a clear colorless volatile liquid which boils at 47°F . If seen at all in the field it would appear as a mist or fog. Some describe the odor as like new mown hay, others as green corn. The vapor density compared to air is 3.4, so it will flow into low places where men usually seek refuge. It is nonpersistent, relatively stable and not rapidly hydrolyzed under favorable field conditions. As it combines with alkalies, soda lime has been used in the gas mask canister as a phosgene absorbent.

Other choking gases are chlorine (no longer used), diphosgene and chloropierin. Diphosgene (DP), trichloromethylchloroformate, is a colorless liquid of low volatility which boils at 262°F and is moderately persistent. It smells like phosgene but can be distinguished by a marked tear gas effect. Symptoms are like phosgene. It may be used in shells or bombs. Chloropierin (PN), a colorless liquid with sweetish odor and intense tear gas effect, would only be used because it is not easily absorbed and a superior gas mask is required for protection against strong concentrations.

The typical blister gas or vesicant is mustard, which was the most effective of all the gases of World War I and is still the standard with which war gases are compared. Mustard gas (HS) (dichloroethylsulfide) was called Yperite by the French and Lost or Yellow Cross by the Germans. In the pure state it is a heavy colorless liquid with slight garlic or horseradish odor and very low volatility. It hydrolyzes very slowly and freezes at 58°F . Although not useful for vapor effect in cold weather it is still valuable for contaminating ground. It is very effective in extremely small concentrations. Mustard is very stable over long periods and may be fired in shells containing considerable explosive. It dissolves in most of the hydrocarbons. It will penetrate rubber. It is de-

stroyed by bleach, the chloramides, and other organic chlorine compounds which are used to decontaminate mustardized surfaces and materials. Strong soaps will destroy weak concentrations on skin and clothing.

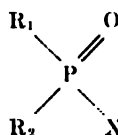
Mustard attacks the skin and all parts of the body. It is a powerful lung irritant. Inhalation of small amounts causes inflammation of the bronchial tubes with destruction of the mucous lining and development of severe bronchial pneumonia. No immediate pain results from contact with the agent and casualties generally develop slowly. The eyes may be affected on long exposures by concentrations as low as one part in 14,000,000 of air, well below the concentration that can be detected by odor. Burns have been caused by contact with ground contaminated with such small amounts that no odor could be detected. Action is cumulative. It is highly persistent, lasting in summer from three days to a week and in winter up to several weeks. Mustard may be used in land mines, as an airplane spray, in bombs, shell and rockets. It is classified tactically as a delayed action casualty gas.

There are several blister gases (vesicants) of varying effectiveness. Lewisite (L) (betchlorovinylchloroarsine), produced by the United States in 1918 but not used, is a highly toxic and irritating compound. It is doubtful in value since it hydrolyzes rapidly. The Germans used ethyldichloroarsine (ED) called "dick" with much effectiveness. Moderately persistent, it is useful in offensive actions where friendly troops may wish to occupy ground a few hours after it has been fired. It is a liquid with a fruity irritating odor. Methylchloroarsine (MD) has been studied by both Americans and Germans but not used in war. It is a highly irritating odorless liquid. The nitrogen mustards are a group of related compounds in which nitrogen is the central atom instead of sulfur. They range from liquids to low-melting solids, are odorless or have faint fishy odor, and are less vesicant than mustard. Their effect on the respiratory tract is severe. They are persistent delayed action casualty gases.

The blood gases are represented by hydrogen cyanide and cyanogen chloride. The French used hydrogen cyanide (HCN) under the name of Vincennite during World War I. Used in artillery shells, it was not satisfactory since it is not cumulative and large concentrations must be delivered in a short time to be effective. Released from large projectors or bombs it might prove useful. It is a nonpersistent quick-acting casualty agent. Cyanogen chloride (CK) was also used by the French, who stabilized it with arsenic trichloride and called the mixture "vitrite". It has a moderate tear gas effect and acts on blood and nerves, but it is not of great importance. It might be used to penetrate the gas mask canister.

The most important war gases to result from World War II research are the "nerve gases" developed by the Germans. They manufactured large amounts of one which they called "Tabun", and loaded into glass-lined bombs and shell. They had two others "Sarin" and "Soman" which they were about to produce as the war ended. All three

are organic phosphorus compounds with the general formula:



The nerve gases are colorless liquids which are odorless, tasteless and very difficult to detect until they have done their damage. They vaporize readily, act rapidly, and affect entire body; death usually occurs within 15 minutes after a fatal amount has been absorbed.

The action of the nerve gases depends on their extraordinary ability to inactivate the enzyme cholinesterase located in nerve and certain important body tissues. This enzyme is present in the body to prevent the accumulation of acetylcholine produced normally in certain body functions. Excess acetylcholine causes abnormal functioning of the nervous system, as for example by paralysis of the nerves that control respiration. The nerve gases all react with and thus inactivate the vital cholinesterase and dangerous accumulation of acetylcholine results quickly. If a victim can be treated quickly with atropine the effects of the acetylcholine are counteracted and recovery follows.

Nerve gases when inhaled cause nausea, diarrhea, and frequently convulsions. Low concentrations cause contraction of pupils of the eyes. The liquid penetrates the skin rapidly and poisons the body. Penetration is even quicker through eyes and mucous membranes. Contraction of the pupils is a warning sign. Protection requires an absolutely tight gas mask and complete set of impermeable clothing. Nerve gas is classed as a quick-acting, nonpersistent, casualty gas. It may be fired in shell and bombs or sprayed from airplanes. (See *Nerve Gases*).

The vomiting gases were developed in World War I to penetrate the mask and cause its removal. Now they are used only for mob control. All are compounds of arsenic, and are generally solids dispersed in aerosol form by heat in smoke candles or grenades. The German Blue Cross, diphenylchloroarsine (DA) fired in grenades, shells, and candles when breathed in very small amounts caused immediate sneezing, then nausea and headache. Diphenylaminechloroarsine (DM) called Adamsite after its discoverer, Dr. Roger Adams, was produced just as World War I was ending. When dispersed from candles by the heat of burning of smokeless powder it forms a bright yellow cloud and has the same effects as DA lasting from 30 minutes to several hours. DM is easier to produce than DA. Diphenylcyanarsine (DC) was introduced by the Germans in May, 1918, as an improvement on DA and was manufactured by the Japanese although not used by them in World War II. All are classified as nonpersistent harassing agents.

The tear gases represent a large class of irritating compounds useful for training and for control of civil disturbances. They have little use in

war. Chloroacetophenone is the standard American tear gas. It is a solid vaporized by heat in grenades or candles or dispersed as a spray when dissolved in chloropierin (CNS), chloroform (CNC) or benzene (CNB), or mixed with explosive in shells or bombs. It has an odor likened to that of locust or apple blossoms. During World War I many tear gases were used. Among them were brombenzylcyanide (BBC) and ethyliodoacetate (SK) of the British, and the German T-Stoff, xylol and benzyl bromide, and 1T-Stoff a brominated methyl ethyl ketone.

No war gases were used in the western war theaters during World War II, but the Japanese used mustard gas against the Chinese in 1941. The Italians sprayed mustard from airplanes on unprotected Abyssinian tribesmen during the Italo-Abyssinian war and the attacks were so successful that the war was ended in a much shorter time than if gas had not been used.

Smokes. Smoke has proved to be a most important chemical agent since its modern development in World War I. It has become a normal military tool in defense and attack to conceal movement of troops, to decrease effectiveness of aimed fire, to screen harbors, shipping, and naval maneuvers, and to obscure cities and prevent aimed bombardment. It has been determined also that smoke clouds will reduce the effect of heat from atomic explosion.

Important smoke agents are FS, a mixture of sulfuric anhydride and chlorosulfonic acid; FM, titanium tetrachloride; HC, a mixture of hexachloroethane, aluminum, and zinc oxide; WP, white phosphorus; and SGF, smoke generator fog. FS and FM are used in shells and bombs and sprayed from airplane tanks. The agent combines with water vapor in the air to form a dense white cloud. HC burns in candles or grenades to yield a white cloud, largely zinc chloride and aluminum oxide. WP, a standard filling for bombs, shell and grenades, burns to form a white cloud of phosphoric acid and is an excellent casualty agent as well as smoke producer and incendiary. Most effective for screening large fixed installations, the mechanical smoke generator produces clouds of minute oil particles which screen effectively for long periods over great distances. The cloud is produced by atomizing and vaporizing SGF, a petroleum oil, with small amounts of water.

Incendiaries. Prior to World War II the United States had not developed incendiary bombs. It was not until the effectiveness of the German incendiary attacks with magnesium bombs on England was demonstrated during the Battle of Britain that development and manufacture was finally authorized. By the end of 1945 the incendiary bomb had proved to be the most efficient munition used.

Thermate bombs (small cylindrical steel casings containing a mixture of iron oxide and aluminum) were hastily produced in time for the successful Doolittle raid on Tokyo, April, 1942. This was the first use of incendiary bombs in an important attack by the U. S. Air Force. The thermate burns to form white-hot iron (4,000°F). Four-pound magnesium bombs with a core of thermate to ig-

nite the body, an alloy of magnesium, aluminum and zinc, soon followed. Small magnesium bombs are clustered in large bundles which open at a predetermined altitude to fall on the target in an effective pattern. Of equal importance are the oil incendiaries. These are thin steel casings or even tanks filled with gasoline, or various blends of motor fuel, generally thickened with napalm or metallic soap, rubber, or other material to decrease speed of burning, improve pattern of the burst and cause fuel to stick to surfaces. Oil bombs are used clustered in small and medium sizes and as large single bombs. Flame bombs are droppable fuel tanks equipped with an igniter, and used generally against personnel. Flame throwers, of little use in World War I, proved very successful in World War II. Thickened fuel gave greater range and better control of the flame.

ALDEN H. WAITT

Cross-references: Carbon (Activated), Aerosols, Toxicology, Noxious Gases, Nerve Gases

CHEMISORPTION see ADSORPTION, CATALYSIS

CHEMISTRY, HISTORY

There are five periods in the history of chemistry. The ancient period comprising the older civilizations of China, India, Egypt, Greece, and their contemporaries to 350 A.D. developed practical arts as in Egypt, and a philosophical approach to the study of matter as in Greece, where a theory of numbers, an atomic theory, and a theory of five elements, earth, air, fire, water and the quintessence were proposed. The alchemical period (350-1500), of which the principal goals were an elixir of life and the philosopher's stone by which base metals could be changed to gold, introduced pure substances and improved techniques. Iatrochemists (1500-1650) devoted their chemical pursuits to alleviation of disease. During the phlogiston period (1650-1774) men postulated a hypothetical matter whose presence was required for combustion and calcination. Gain in weight by calcination of metals led to a search for a very light material and subsequent discovery of gases, one of which was oxygen, and the answer to the problem. This is the date when modern chemistry begins.

When qualitative and quantitative analysis, the first fields of chemistry to be developed, had identified enough pure substances, inorganic chemistry grew in scope. Organic chemistry was very little understood until 1828 when the synthesis of urea by Wöhler proved clearly that the "vital force" thought to be imperative to produce compounds which occurred in living matter was not needed. Meanwhile reliable physical chemical measurements began with the gas laws of Boyle (1660), Charles (1785), Gay-Lussac (1808), and Dalton (1807). Dalton's Atomic Theory (1807), postulated after the Laws of the Conservation of Mass and Definite Proportions were tacitly assumed, stimulated the 19th century effort to determine accurate atomic weights, ideas for combination as expressed in valence, and the studies of molecular

structure until the three-dimensional models appeared.

Gradual determination of physical properties of the elements indicated a periodicity of property expressed by the Periodic Law which has withstood the onslaught of the discovery of the inert gases, the transuranic elements, and isotopes. The duties of the atoms, increased by a need to explain radiation and radioactivity, necessitated proposal and discovery of the subatomic particles which make up the nucleus and outer electrons of the atom.

Twentieth century chemistry has narrowed into units such as instrumental analysis, biochemistry, chemical engineering, and colloids. Chemistry has progressed from an assembly of facts to a statement of laws, and thermodynamics of chemical reactions to a study of atomic structure. It is also an age of practical applications which, if not the product of an elixir, do contribute to an improved standard of living. Man has learned to surpass nature as he explores the methods by which living matter is produced. To create a better environment, empirical studies of the past have been replaced by an assurance that any type of matter may be synthesized or analyzed with time and effort.

VIRGINIA BARTOW

Cross-references: *Alchemy, Atoms, Gas Laws, Periodic Law*

CHEMOTHERAPY, *see* ANTIBIOTICS, PHARMACEUTICALS

CHEMURGY

Chemurgy is the linking of agricultural, scientific, and industrial efforts to improve active co-operation between these branches of a nation's economy for their mutual benefit. This definition, arrived at in 1952 by the executive committee of the National Farm Chemurgic Council, is more inclusive than some previous definitions because of the expanded scope of the chemurgic idea. The term "chemurgy" was first used in 1934, having been coined from the combination of two Greek words (*chemi* = chemistry + *ergon* = work). The chief objectives of Farm Chemurgy can be listed under four heads: (1) new, nonfood uses for farm crops, their residues and byproducts; (2) new and profitable uses for previously unused plant materials; (3) new crops that farmers may grow profitably; (4) more valuable uses for presently used crops through chemurgic upgrading. The scope of chemurgy also includes the practical utilization of the products of the forest, the sea, and the desert as well as those of the farm.

The farm chemurgic movement was formally initiated May 7-8, 1935 when a group of industrialists, scientists and agriculturalists met in Dearborn, Michigan with the primary objective of promoting research in the finding of new uses for those crops that at the time were being over-produced. A short time later this group became known as the National Farm Chemurgic Council. and in 1955 the name was changed to The Council for Agricultural and Chemical Research. This organization sponsors the chemurgic movement and

publicizes current developments through national and regional meetings and its monthly publication, *Chemurgic Digest*.

During the 1930's the emphasis often was more or less on the salvaging of industrial raw materials from those farm food crops of which there were great surpluses. Now there is a growing realization, especially when considering the world at large, that there ought to be more concern about the ability of agriculture to produce sufficient products in view of the increasing population, raised living standards in many areas of the world, and the deterioration of the soil in many areas. It is a proper function of chemurgy to promote all means of making world-wide agriculture, forestry and other biological resources as productive as possible in the needed food and chemurgic raw materials. It is important that land now used to produce commodities that are surplus both for food and profitable chemurgic use be planted to adaptable and profitable new crops which can be so used.

The following are some selected topics chosen to illustrate the chemurgic idea.

Our civilization requires enormous amounts of cellulose in the form of natural vegetable fibers, various kinds of paper, derived products, such as rayon and acetate rayon fibers, cellulose nitrate, acetate and other esters for protective coatings, plastics, and photographic films, and the more highly nitrated cellulose as an explosive. The derived products were originally prepared from cotton linters but now, except where high purity is required, such as in cellulose esters for photographic film, they can be made from wood pulp that is more highly purified than that used for paper making.

The chemurgic utilization of farm residues is often profitable when sufficient quantities of these materials can be conveniently collected at the factory. Satisfactory paper and paper board can be made from sugar cane bagasse and wheat straw. Wall board can be made by the compression of corn stalks and similar materials. Furfural, a volatile aldehyde, is made on a large scale by heating pentosan-containing materials such as oat hulls, cotton seed hulls, corn cobs, etc. with dilute mineral acid. Furfural has many uses in the chemical industry. It can be converted into both adipic acid and hexamethylenediamine and the condensation of these two chemicals with the elimination of water yields 66 nylon.

As a possible new source of cellulose suitable for paper making, bamboo can be grown on marginal land in the southern states to yield six or seven times as much cellulose per acre per year as a southern pine forest.

Oilseeds are good new chemurgic crops for several reasons. Local production of oils having the various desired characteristics would make the country self sufficient in times of emergency. The meal left after removal of the oil is usually rich in proteins. Such meals, except a few such as castor and tung which contain toxic substances, are good protein supplements for animal feed. The proteins are also used in the making of plastics and adhesive and in some cases vegetable protein fibers.

Certain oilseed crops are often well adapted to the soil when new crops are needed to replace those no longer practical.

The introduction of the soybean into U. S. and its development into a major crop is one of the triumphs of chemurgy.

The growing of tung trees (*Aleurites fordii*) is an established industry in several of the Gulf states, but this does not satisfy the demand for the valuable oil. Tung oil consists largely of glycerides of eleostearic acid having conjugate unsaturation, and is hence a drying oil which polymerizes readily. It is much desired for use in varnish.

The castor plant (*Ricinus communis*) has been introduced into the U. S. Castor oil is largely a glyceride of ricinoleic acid. Its traditional medical use is a very minor one. The oil can be converted into a good lubricant. Removal of the hydroxyl radicals together with hydrogen atoms yields dehydrated castor oil having conjugate unsaturation; hence it is a good drying oil. Ricinoleic acid can be cleaved into undecylenic acid plus heptaldehyde by pyrolysis or into sebacic acid plus 2-octanol by heating with alkali. These compounds are used as intermediates in making various fine chemicals including certain flavors and perfumes.

Sesame (*Sesamum indicum*) was one of the first oilseeds cultivated by man as a food. Efforts are being made to establish it as a new crop in U. S. In the usual sesame plant there is lack of uniformity of maturity and there is dehiscence which allows shattering of the seeds. Since manual harvesting is practical only where labor is cheap, the above defects must be overcome without decrease in the yield or quality of the seeds by breeding so that mechanical harvesting is possible. Such desired new variety appears to have been produced. The oil is a high-grade nondrying oil.

Safflower (*Carthamus tinctorius*) is another oilseed introduced as a new source of drying oil.

Pesticides, which include insecticides, fungicides, herbicides and rodenticides, are important because without them many agricultural and chemurgic projects could be rendered ineffective. The pesticides derived from plant materials are of special chemurgic interest.

Several of the antibiotics have been used to protect plants against bacterial and fungus diseases.

Red squill (*Urginea maritima*) and strychnine from *Strychnos* spp. have long been used as rodenticides.

The principal insecticides extracted from plants are: nicotine, nornicotine and anabasine from *Nicotiana* spp., anabasine also from *Anabasis aphylla*; rotenone and related compounds from *Derris*, *Lonchocarpus*, *Thephrosia* and *Mundulea* spp.; pyrethrum from *Chrysanthemum cinerariaefolium*; ryania from *Ryania speciosa*; and sabadilla from *Schoenocaulon officinale*. Several insecticides are synthesized from constituents of turpentine or pine oil and some of the important ones of this type are toxaphene (a chlorinated camphene), Strobane (chlorinated terpenes) and isobornyl thiocyanacetate.

Pyrethrum is markedly synergized by certain compounds. Sesamin, a minor constituent of sesame oil was the first synergist discovered. Re-

cently sesamol, another minor constituent of this oil, was found even more effective. Piperine, the alkaloid of black pepper, was also found effective. All these natural synergists contain the methylenedioxyphenyl nucleus in their structures and this appears to be necessary for activity. Several effective synthetic synergists containing this nucleus are piperonyl butoxide, *n*-propyl isome, *n*-octyl sulfoxide of isosafrole, and piperonyl cyclonene. Since the methylenedioxyphenyl nucleus is not profitably synthesized, it is necessary to rely on plant sources for this portion of the molecule. Safrole from the high boiling fraction of camphor oil or from the oil of *Ocotea cymbarum* is the starting material used.

It is remarkable that all of our major crops and most of our minor crops were brought into use in prehistoric times. Chemurgic opportunities exist for finding uses for those plants which are now useless as may be seen from the following examples. The creosote bush (*Larrea divaricata* Cav.), a widespread desert weed, has been found to contain nordihydroguaiaretic acid, effective as an antioxidant for fats, and other extractives. The extracted residue is then suitable for cattle feed. Jojoba (*Simmondsia californica*), a wild desert shrub, produces seeds containing a liquid wax similar to sperm oil and which can be hydrogenated to form a replacement for carnauba wax. Steroid sapogenins from several plants are useful as starting materials for the synthesis of cortisone.

It is the ideal of chemurgy that the needs of mankind be supplied as much as possible by the renewable plant material grown from the soil rather than by the irreplaceable mineral resources.

EDWARD A. PRILL

Cross-references: Cellulose, Vegetable Oils, Pesticides, Agricultural Chemistry

CHLORATES

Chlorates are manufactured commercially by electrolysis of aqueous solutions of the chlorides. Sodium, potassium and barium chlorates constitute the most important chlorate compounds. The chemistry of electrolysis to form chlorates involves first the formation of chlorine, which then produces mixtures of HOCl and the metal chlorite. These then react to give the chlorate and chlorite. Further oxidation yields the perchlorates. Of the two commercial processes the alkaline electrolytic process has a theoretical 100% efficiency and the acid one is characterized by high electrochemical efficiency. Other metal chlorates are prepared by double decomposition from barium chlorate and the metal sulfates.

The most characteristic property of chlorates is their oxidation potential caused by their relatively easily effected decomposition to the chloride and free oxygen. Mixtures of chlorates (in appropriate "oxygen balance") with organic materials, metals (Al, Mg, As, Cu, etc.), carbon, phosphorus, and sulfur are generally powerful and more or less dangerous explosives. Chloric acid solutions are very reactive and are able to dissolve various metals (Cd, Cu, Fe, sodium amalgam, etc.) and decompose organic materials rapidly, often with

flame. Esterification of AcOH in EtOH is greatly accelerated by $\text{Cu}(\text{ClO}_2)_2$.

The oxidation potential is responsible for the strong toxic effects of chlorate. Thus chlorate penetrates the erythrocytes and attacks the hemoglobin, converting it to methemoglobin through an autocatalytic process in which reduction of the chlorate is a necessary step. Mere traces of chlorate in the soil are injurious to wheat and other plants.

While relatively high sensitivity toward explosion is achieved with chlorates by admixture with combustibles, the decomposition of the pure metal chlorate to the chloride and free oxygen is itself exothermic and may lead to explosion. Thus KClO_3 and NaClO_3 generate 16 kilocalories per mole in decomposition, and the spontaneous explosion of potassium chlorate is not uncommon. Decomposition of chlorates may be catalyzed or accelerated by contaminants of various types, for example, manganese dioxide and even fine sand or powdered glass.

The chlorates are more powerful oxidizing agents than the chemically similar bromates and iodates. Indeed, KClO_3 will oxidize iodine chloride to KIO_3 with evolution of chlorine, and will oxidize bromine to the bromate stage. (Chlorine is not oxidized by iodates or bromates, but iodine is converted to iodate by chlorine). The power of chlorates as oxidizing agents is further illustrated by the fact that KClO_3 will oxidize ammonia to KNO_3 with the liberation of KCl and chlorine. It must therefore be a stronger oxidizing agent even than the corresponding nitrate.

Monovalent metal chlorates do not add water of crystallization, but the bivalent ones add from one to six molecules of water per molecule of chlorate. Trivalent chlorate salts, while almost unknown, probably have considerable water of crystallization in the solid state. On heating at sufficiently low temperatures the hydrated salts lose their water of crystallization without further decomposition showing that they are salts of a strong acid. In all these respects the chlorates are very similar to the corresponding nitrates.

The primary uses of chlorates are in the manufacture of explosives, fireworks and matches. One of the oldest and still useful detonators (the fuse cap) is based on mixtures (90/10 and 80/20) of mercury fulminate and potassium chlorate. These detonators are more powerful, cheaper and safer than pure mercury fulminate. Chlorates are also used in insecticides and for medicinal purposes.

Like perchlorates, nitrates and other oxidizing agents, chlorates in combination with combustibles of all types constitute a serious fire and explosion hazard. Such mixtures are frequently quite sensitive to flame, shock and friction and must thus be handled cautiously.

M. A. COOK

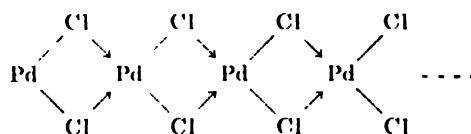
Cross-references: *Chlorine, Explosives, Oxidation*

CHLORIDES

The simple chlorides include that group of compounds which may be regarded as formal deriva-

tives of hydrogen chloride, HCl , and which may be represented by the general formula MCl_n where M represents a metal, a nonmetal, an organic or inorganic radical, or a complex. Strictly speaking, M should have a lower electronegativity than chlorine. Thus, compounds having a great range in physical and chemical characteristics are included in this group. If M represents a metal of very low electronegativity, such as one of alkali metals, the resulting chloride is a typical ionic compound with a crystal lattice consisting of an indefinitely extended three-dimensional array of positive and negative ions but containing no finite molecular groups. Silver, thallous, and cuprous chlorides belong to this group also. A similar situation obtains when M represents a complex ion such as NH_4^+ or $\text{Co}(\text{NH}_3)_6^{+++}$, except that the positive ion positions in the ionic lattice are occupied by complex rather than simple ions.

The chloride ion is, however, sufficiently polarizable that when M becomes a metal of somewhat higher electronegativity than the alkali metals, covalent bonding may begin to play an important role in the crystal lattice. This effect manifests itself by the appearance of more or less covalent complexes indefinitely extended in one dimension (chain-type structures) or in two dimensions (layer-type structures). An example of the chain-type structure is palladium chloride (PdCl_2) which has the indefinitely extended chain structures of the type



in its crystal lattice. Examples of chlorides having layer-type structures include the chlorides of $\text{Cd}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Ni}(\text{II})$, Mg , Zn , $\text{Mn}(\text{II})$, $\text{Cr}(\text{III})$, and $\text{Fe}(\text{III})$.

As the differences in electronegativity between M and Cl decrease, the trend toward covalent bonding increases. This factor, combined with steric and other considerations, results in many chlorides having molecular type lattices composed of finite, discrete molecules. The configurations of these molecules depend upon the bonding orbitals available on the atom M . In some instances the molecular formulas do not correspond to the empirical formulas. Thus, aluminum chloride vapor is composed of Al_2Cl_6 molecules. Ferric chloride vapor is likewise composed of dimers, Fe_2Cl_6 .

The molecular type chlorides are generally characterized by weaker crystal lattices, lower melting points and higher volatilities than the previously mentioned types of chlorides. Many molecular chlorides exist in the liquid phase at room temperature. The molecular chlorides include the organic chlorides such as CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$, and CHCl_3 .

A large number of chlorides are known in which more than one element is combined with chlorine in a given compound. Such complex chlorides may be represented by the general formula $\text{A}_x\text{B}_y\text{Cl}_z$. This includes the situation where A and B refer to the same element but in different oxidation

states; e.g. TiCl_2 is really $\text{Ti}^{\text{IV}}\text{Ti}^{\text{III}}\text{Cl}_4$. The variety of complex halides is very great. There are four chief structural possibilities for the complex halides:

- A, B, and X forms an infinite 3-dimensional array of ions in which no finite or indefinitely extended chain-type or layer-type complex may be distinguished. There are few examples of this among the complex chlorides but it is quite common for the fluorides.
- B and X form layer complex anions. Again no structures of this type have been found among the complex chlorides.
- B and X form chain complex anions. Examples include NH_4CdCl_3 , $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$, $\text{K}_2\text{SnCl}_4 \cdot \text{H}_2\text{O}$, and RbCdCl_3 .
- B and X form finite complex anions of the formula $[\text{B}_n\text{X}_n]^{(n-x)-}$ where n is the oxidation number of B. There are a great many examples of these among the chlorides.

The preparatory methods and reactions of the various chlorides cover an exceedingly wide range. It may be pointed out, however, that since chlorine in virtually all the chlorides is in its lowest oxidation state, the chlorides are in general susceptible to the action of strong oxidizing agents to yield molecular chlorine or in some instances even higher oxidation products.

HARRY H. SISLER

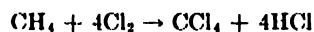
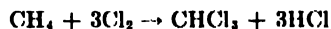
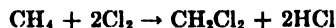
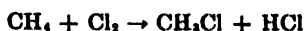
Carbon Tetrachloride

Carbon tetrachloride (CCl_4) requires special mention because of its peculiar properties. It is a liquid of specific gravity 1.58 with a characteristic sweetish odor. There has been considerable divergence of opinion about its toxicity, but it is now generally agreed that it presents a definite toxic hazard. The Manufacturing Chemists Association requires a warning label on shipments of this material. While it is often used as a fire-extinguishing agent, it should be remembered that heat will cause it to decompose to form phosgene. In freely ventilated areas above ground, this is probably a minor factor, but in enclosed areas that are poorly ventilated, it may be dangerous. Its chief use is as a solvent, especially in dry cleaning. In all industrial and large-scale indoor applications, adequate ventilation is essential. Since its fumes are heavy, special attention should be given to ventilating low areas where pockets of toxic gases may accumulate. [Ed.]

Cross-references: *Chlorine, Chlorinated Hydrocarbons, Oxidation*

CHLORINATED HYDROCARBONS

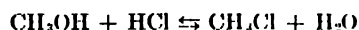
Chlorinated hydrocarbons are hydrocarbons in which one or more of the hydrogen atoms has been replaced by chlorine. Two general methods, chlorination and hydrochlorination, are used to prepare them. In most cases chlorination by *substitution* involves the reaction of elementary chlorine with hydrocarbons. The chlorination of methane is a good example of this process:



The composition of the reaction products varies with the conditions. The reactions are highly exothermic so good temperature control is essential. Other chlorinating agents besides chlorine can be used such as phosphorus pentachloride, sulfuryl chloride, thionyl chloride, sulfur dichloride, and antimony pentachloride. Some of these chlorinating agents also act as catalysts in chlorination with elementary chlorine.

In chlorination by *addition*, chlorine reacts with unsaturated hydrocarbons to form dichloro derivatives. The addition of chlorine to ethylene to form ethylene dichloride is a good example. Chlorine can also react with unsaturated chlorine compounds by addition; the formation of 1,1,2-trichloroethane from vinyl chloride occurs in this way.

Hydrochlorination. Hydrogen chloride can react with a number of organic compounds by *substitution*. In the majority of cases, however, the substitution is with alcohols. The reaction in the case of methyl chloride is as follows:



Since this reaction is reversible it is made to proceed to the right by removing the methyl chloride as fast as formed and by maintaining a high concentration of methanol and hydrogen chloride. Ethyl chloride and butyl chloride are made industrially by this process from their respective alcohols. Hydrogen chloride will also react by substitution with other organic compounds such as amines, ethers, esters, acids, aldehydes and ketones to give chlorinated hydrocarbons. Due to economic considerations, these reactions are seldom used industrially.

The *addition* of hydrogen chloride to unsaturated compounds to produce chlorinated hydrocarbons is of considerable importance industrially. For example, hydrogen chloride will add to ethylene to form ethyl chloride and to acetylene to form vinyl chloride.

Physical Properties. The stepwise substitution of chlorine for hydrogen in hydrocarbons in general increases the boiling point, melting point, density and refractive index. One outstanding exception to this generalization is the decrease in melting point in going from benzene to monochlorobenzene. A reduction in molecular symmetry is believed responsible for this anomaly. The substitution of one hydrogen by chlorine in a hydrocarbon generally produces only a slight drop in flammability. Further substitution then produces a rapid drop. Fully chlorinated derivatives are nonflammable. The chlorinated hydrocarbons are generally good solvents for fats and oils and poor solvents for water and polar substances.

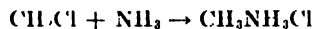
Chemical Properties. The chlorinated hydrocarbons are moderately reactive chemicals and show a wide variation in reactivity with structure.

Pyrolysis. The position of the chlorine in ali-

phatic chlorinated hydrocarbons has a marked effect in pyrolysis. The stability decreases in proceeding from primary to secondary to tertiary. The primary chlorides decomposes only at temperatures in the range of 400-500°C. The completely chlorinated derivatives have about the same stability. The unsaturated chlorinated hydrocarbons show low stability at low chlorine content and high stability when completely chlorinated. The aromatic chlorides all show remarkable heat stability. For example a bright red platinum wire is required to decompose chlorobenzene. The chlorinated alicyclic hydrocarbons have somewhat the same stability as the primary saturated paraffin derivatives and in both cases hydrogen chloride is nearly always produced as a decomposition product.

Hydrolysis. The rate of hydrolysis of saturated aliphatic chlorinated hydrocarbons increases from primary to tertiary derivatives. The primary chlorides are converted chiefly to alcohols. Secondary chlorides give some alcohols but mostly olefins. Tertiary chlorides give olefins almost completely. The chemical properties of the saturated aliphatic derivatives differ strikingly from the aromatic and unsaturated derivatives. This is illustrated in rates of hydrolysis. For example methyl chloride and benzyl chloride are readily hydrolyzed by boiling dilute sodium hydroxide solution, whereas chlorobenzene requires solid caustic at about 300°C. Any chlorine adjacent to a double bond shows increased chemical stability. In the methane series methylene chloride is considerably more stable than the other members. This increased chemical stability of methylene chloride, trichloroethylene and tetrachloroethylene has stimulated their use as industrial solvents. They show less hydrolysis, corrosion of metals and toxicity than such old chlorinated solvents as chloroform and carbon tetrachloride.

Reactions with amines. The reaction of chlorinated hydrocarbons with ammonia and amines is of considerable importance in synthetic organic chemistry. The usual reaction is one of addition, forming an amine chloride. The reaction is illustrated with methyl chloride and ammonia:



If alkali is present the free amine is formed,



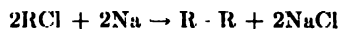
which can react with more methyl chloride forming higher amines. The ultimate product, when excess alkali is present is tetramethyl ammonium hydroxide.

These reactions occur quite readily with most primary monochlorinated hydrocarbons. Secondary and tertiary derivatives react with ammonia and amines but generally by hydrogen chloride removal and olefin formation. Some polychlorinated hydrocarbons will react with ammonia to form amines if one chlorine is singly attached to carbon. The formation of ethylene diamine from ethylene dichloride and ammonia is an example.

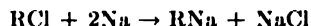
Chlorinated aromatics will react with ammonia at high temperatures and pressures to form

amines. For example chlorobenzene will react with ammonia at about 200°C, in the presence of a catalyst of copper oxide and chloride to form aniline.

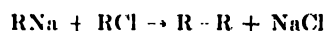
Reactions with metals and metal salts. Primary monochlorinated hydrocarbons in general react with metals such as sodium, potassium, and lithium to form hydrocarbons, by a Wurtz reaction,



This reaction proceeds through the intermediate formation of a metal salt of the hydrocarbon,



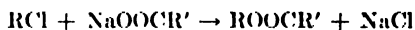
followed by reaction of this salt with more of the chloride



The primary monochlorinated hydrocarbons react quite readily with several types of metal organic compounds. Some examples are the reaction with sodium alcoholates to form ethers (Williamson synthesis of ethers):



the reaction with the sodium salt of organic acids to form esters,



and the reaction with sodium cyanide to form nitriles,



Production and Uses. The production of chlorinated hydrocarbons is given below. The first four are mostly captive. The largest captive use for *ethylene dichloride* is as a coupling agent in antiknock fluid. *Ethyl chloride* has two important captive uses - the manufacture of tetraethyl lead and of ethyl cellulose. *Vinyl chloride* monomer, which includes some vinylidene chloride, finds its major use in vinyl plastics. The major captive uses for chlorobenzene are in the manufacture of phenol, aniline and nitrated chlorobenzenes.

	Production (millions of pounds)			
	1951	1952	1953	1954
Ethylene dichloride	436	436	520	--
Ethyl chloride	419	442	520	--
Vinyl chloride monomer	431	321	401	--
Chlorobenzene	471	382	377	327
Trichloroethylene	--	270	323	207
Carbon tetrachloride	244	219	260	234
Tetrachloroethylene	110	106	153	158
Methylene chloride	40	55	64	--
Benzene hexachloride	117	86	60	59
Methyl chloride	37	34	40	--
Chloroform	26	22	26	--
Chloroparaffins	44	47	33	--
Benzyl chloride	11	10	10	--

Trichloroethylene and *tetrachloroethylene* are used almost entirely as solvents for dry cleaning, metal degreasing and extraction of fats and oils. At one time carbon tetrachloride was very important in these fields but because of greater hydrolysis and toxicity it has lost ground. The major use for carbon tetrachloride today is in the manufacture of fluorochloro methanes, which in turn are used as refrigerants and aerosol propellants. *Methylene chloride* is used mainly in paint and varnish removers. *Methyl chloride* has three important uses, one as a catalyst solvent in Butyl rubber production, another as a reagent in silicone production and the third as a methylating agent. *Chloroform* is used as a solvent and as a chemical reactant.

Benzene hexachloride is produced almost entirely for its gamma isomer content, which is an excellent insecticide and miticide. *Benzyl chloride* is used primarily as a chemical reactant. The chlorinated paraffins are important as plasticizers, mildew proofing and flame proofing agents.

P. J. EHMAN

Cross-references: *Solvents, Hydrocarbons*

CHLORINE

Chlorine is an element with atomic number 17, atomic weight 35.45; it is in Group VII B of the Periodic System. It is a gas at ordinary temperatures and is never found free in nature. It has the following physical properties:

Boiling point: -34.5°C .

Compressibility of liquid: 0.0118% per unit vol. per 1 atm. pressure increase at 20°C .

Critical density: 573 g. per liter.

Critical density: 76.1 atm.

Critical temperature: 144°C .

Density: gas, 3.214 g./l. at 0°C , (1 atm); liquid 1468 g./l. at 0°C .

Freezing point: -100.98°C .

Heat of fusion: 22.9 g. cal./g.

Latent heat of vaporization: 68.8 cal./g.

The modern chlorine industry, not unlike other chemical enterprises, is greatly indebted to the science of the late 18th and early 19th centuries. Scheele, in 1774, prepared gaseous chlorine by the action of hydrochloric acid on manganese dioxide. Northmore prepared the first liquid chlorine in 1805. Sir Humphry Davy, in 1807, by the decomposition of fused salts with an electric current, was able to produce sodium and potassium, and in 1810 demonstrated that chlorine is an element; discarding the old name "oxygenated or phlogistonated muriatic acid" he gave the name chlorine (from Greek word for "green") and sealed the doom of the phlogiston theories. In 1833 Faraday discovered and set forth the laws for the action of electric current on salt solutions.

As a gas, chlorine is never shipped in commerce except for short distances in pipe lines. As a liquid it is shipped daily in very large quantities in cylinders loaded not in excess of 150 pounds; in containers loaded to 1 ton; by motor trucks in cylinders and in containers loaded to 1 ton; in tank barges loading as much as 600 tons; in tank cars holding 15, 16, 30 and 55 tons, and for short

distances in pipe lines of varying capacity. All types of containers used in the transportation of liquid are strictly governed by the Regulations and Specifications of the United States Coast Guard or the Interstate Commerce Commission and in some cases by the codes of States. In practice there is no important difference in marking and other requirements for motor trucks and rail carrier shipments between interstate and intrastate commerce.

The physiological response to various concentrations of chlorine gas is set forth in the following table from the Bureau of Mines Technical Paper No. 248.

Effect	Parts of Chlorine Gas per Million Parts of Air (by Volume)
Least detectable odor.	3.5
Least amount required to cause irritation of throat	15.1
Least amount required to cause coughing.	30.2
Least amount required to produce slight symptoms (of poisoning) after several hours exposure	1.0
Maximum amount that can be breathed for one hour without serious effects.	4.0
Amount dangerous in 30 minutes to one hour	40-60
Amount likely to be fatal after a few deep breaths	1000

The uses of chlorine are legion, as it is used as a tool of manufacture and as a component of a finished product. The first American use of chlorine was in the sanitary field, and that use has long been considered indispensable in the sanitation of water intended to be made potable. There are also many applications in the sanitation of industrial wastes, sewage and swimming pools. At a very conservative estimate chlorine is applied in sanitation at 15,000 such locations in the United States. The bleaching of pulp, the production of carbon tetrachloride, chlorobenzenes, ethylene glycol, synthetic glycerine, tetraethyl lead and trichloroethylene consume large quantities. There are many other reactions of chlorine with organic substances consuming chlorine. The present American production of chlorine gas is about 8,400 tons per 24 hour day. Of this amount about one half is liquefied and shipped. All nations of the modern industrial type have and use chlorine-producing facilities.

Chlorine is generally produced by the electrolysis of water solutions of sodium chloride in an electrolytic cell of the Hooker, Vorce, or Allen-Moore type. There is also a small production by electrolysis of potassium chloride, the electrolysis of fused sodium chloride designed for the production of metallic sodium, and also a process incidental to the production of nitrate of soda. When sodium chloride or potassium chloride solutions are subjected to electrolysis, there are three products; caustic soda or caustic potash, chlorine and hydrogen. If fused sodium chloride is used, there are two products: chlorine and metallic sodium. The economic aspects of these matters are complicated because the products are dangerous substances requiring great care in handling; by marketing conditions; and by changing uses. The location of a chlorine plant is not a simple matter.

The ideal location would be one providing cheap power, salt or brine, transportation and water, skilled labor and consumption on the spot or nearby suitable markets. There is no such location. All present locations have some but not all such advantages.

Chlorine has always been an important factor in the production of war gases, and to the extent of use of such gases the chlorine plants are an important element of the national defense. (Based on information supplied by The Chlorine Institute, Inc., R. J. Baldwin, Secretary)

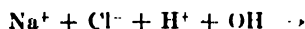
GEORGE L. CLARK

Electrolytic Cells

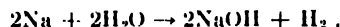
For commercial production of caustic soda, sodium, and chlorine reaction chambers called "cells" are used. These may be of many types, though the Hooker, Allen-Moore, Voree and Nelson cells are most extensively used. These are all of the diaphragm type; a cell having a mercury cathode is also used to some extent (Castner, Sorensen).

The essential parts of an electrolytic cell are shown in Fig. 1. The current, which is always direct current, is said to enter at the anode and to leave at the cathode. In a brine, there are present sodium ions (Na^+) and chloride ions (Cl^-), as well as ions resulting from the ionization of water, *i.e.*, the hydrogen ion (H^+) and the hydroxyl ion (OH^-). After the current is applied, the chloride ions give up their negative charge (one electron) and become yellow chlorine gas, Cl_2 . The hydrogen ions acquire an electron each at the cathode, and form the hydrogen molecule (hydrogen gas). There are many more Na^+ ions than H^+ ions present at any time, but the single potential for hydrogen is lower than that for sodium. As soon as the hydrogen ions present have deposited, more are formed by ionization of the water molecule, a process which takes place at a rate approaching the speed of light. The Na^+ ions thus remain undisturbed during the action of the current on the brine. The OH^- ions, constantly formed by the ionization of the water, accumulate at a rate which

equals that of chlorine ion discharge, so that the Na^+ ions are matched in number by the newly formed OH^- ions. The reaction may be written:



This is the process which goes on in the diaphragm cell. In the mercury cell, the deposition of hydrogen ions at the mercury cathode does not occur, because the mercury cannot accept them; here, the Na^+ ion functions, by acquiring an electron and dissolving as sodium metal in the mercury. In a second chamber, the amalgam first formed is "denuded" of its sodium, forming with water Na^+ again, and liberating hydrogen, which in turn leaves an equivalent number of OH^- ions to form the caustic soda in solution:



Diaphragm cells are so connected that the current leaving at the cathode of one cell enters at the anode of the next. The path of the current lies through the metallic bar to the anode, through the liquid to the cathode opposite, through a metallic connection to the next anode, and so on to the last cathode, which is connected to the terminal at the generator. As it passes through the metal, the current causes no chemical change; but as it goes through the brine, the decomposition takes place which has been described. In the Townsend cell, caustic gradually accumulates near the cathode; to prevent it from diffusing toward the anode, a wall may be placed in the cell, forming two compartments. The wall allows slow passage of the solution and free passage to the sodium ions; by keeping the level in the anode chamber higher than in the cathode chamber, the hydrostatic flow is toward the cathode, nullifying the diffusion tendency of the NaOH toward the anode. The permeable wall diaphragm is usually asbestos fibers supported on an iron screen.

E. R. RIEGEL

Cross-references: *Electrolysis, Bleaching, Chemical Warfare*

CHLOROHYDRINS

Aliphatic organic compounds which are both alkyl chlorides and alcohols are called chlorohydrins. Those most frequently encountered contain one chlorine atom and one hydroxyl group on adjacent carbon atoms.

Preparation. A general method of preparation is the addition of hypochlorous acid to alkenes. Addition to an unsymmetrical alkene yields predominately a product in which the hydroxyl group is attached to the carbon atom poorest in hydrogen. Thus, reaction of hypochlorous acid with 1-alkenes gives chlorohydrins of the structure $\text{RCH(OH)CH}_2\text{Cl}$. The initial step in this reaction is an attack on the electron-rich carbon atom of the double bond by an electrophilic reagent. The formed intermediate is subsequently decomposed by a water molecule or in alkaline medium by hydroxide ion. The active electrophilic reagent in hypochlorous acid, acidified with sulfuric or per-

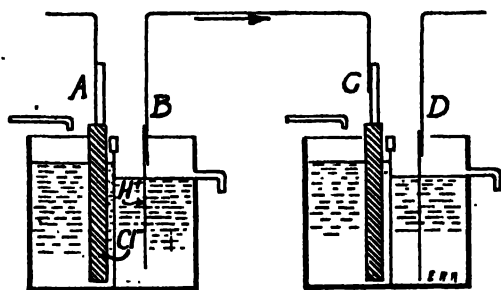


FIG. 1. Cells for the electrolysis of solutions of sodium chloride in water. The chloride ion, Cl^- , forms chlorine gas at the anodes, marked A and C; the hydrogen ion, H^+ , forms hydrogen gas at the cathodes; the latter are marked B and D. A diaphragm divides the anode brine compartment from the cathode compartment.

chloric acids, is the chlorinium ion Cl^+ for reactive alkenes and the hypochlorous acidium ion ClOH_2^+ for very reactive alkenes such as 2-methylpropene. In weak acidic solutions the effective electrophilic reagent is hypochlorous acid and chlorine monoxide.

Chromyl chloride in carbon tetrachloride reacts with 1-alkenes to form chlorohydrins of the type $\text{RCHClCH}_2\text{OH}$ and with cyclohexene to form trans-2-chlorocyclohexanol. Presumably the chromyl chloride donates a positive CrO_2Cl fragment to the alkene to form a three or five-membered cyclic intermediate which reacts in a subsequent step with chloride ion; hydrolysis of this product gives the chlorohydrin. Industrial processes for producing chlorohydrins from alkenes include the addition of hypochlorous acid indirectly by the use of monochlorourea or *t*-butyl hypochlorite, as well as the passing of chlorine and an alkene into water under controlled conditions of temperature and concentration.

Cyclic ethers may easily be converted to chlorohydrins by treatment with hydrochloric acid. The rate of reaction is proportional to the concentration of the cyclic ether, hydrogen ion and chloride ion. Inversion is observed to accompany the opening of the oxide ring. These kinetic and stereochemical results of opening the oxide ring by hydrochloric acid are best explained by a mechanism involving the addition of a proton to the epoxide oxygen to form the conjugate acid of the oxide, followed by a nucleophilic displacement by chloride ion. The opening of unsymmetrically alkyl substituted ethylene oxides by hydrochloric acid usually results in mixtures of the two possible chlorohydrins. In some cases particularly with aryl substituted ethylene oxides a single product is formed.

Chlorohydrins may also be formed by the treatment of various glycols with chlorinating agents such as hydrochloric acid, thionyl chloride or sulfur chloride. These methods are often complicated by the occurrence of disubstitution. Other methods of preparation of chlorohydrins include the reaction of Grignards with chloroaldehydes and chloroesters and the reduction of chloroketones with aluminum ethoxide. Chlorohydrins are also made successfully by the reduction of chloroacids, chloroesters and chloroacid chlorides by lithium aluminum hydride.

Reactivity. Kinetic studies on the reaction of some chlorohydrins with water established that 4-chloro-1-butanol reacts 1000 times as fast as 2-chloroethanol and 200 times as fast as 3-chloro-1-propanol. Tetrahydrofuran was the main reaction product of 4-chloro-1-butanol with water, while ethylene glycol and trimethylene glycol are the only products in the hydrolysis of 2-chloroethanol and 3-chloro-1-propanol.

Treatment of 2-chloroethanol with sodium hydroxide yields ethylene oxide. The reaction is first order with respect to hydroxide ion and first order with respect to the chlorohydrin. A mechanism which accounts for the kinetics and the formation of the epoxide involves a two step process. The first step is a rapid equilibrium between the hydroxide ion and the hydroxyl group of the chlo-

rohydrin followed by a rate-determining displacement of chloride ion from the chloroalcoholate ion. The rate of formation of ethylene oxide thus depends upon the acidity of the chlorohydrin and upon the reactivity of the chloroalcoholate ion formed. Reaction of hydroxide ion with 4-chloro-1-butanol also gives a cyclic ether, tetrahydrofuran, and follows second-order kinetics.

The reaction of 3-chloro-1-alkanols with hydroxide ion is quite slow compared to 2-chloroethanols and 4-chloro-1-butanols and the yields of trimethylene oxides are usually low, the predominant reaction being elimination and some substitution. The elimination reaction is favored by the inductive effects of both the chlorine atom and the hydroxyl groups affecting the same beta carbon atom favoring the release of a proton. *Gem*-dialkyl substitution on the hydroxyl bearing carbon seems to aid trimethylene oxide formation. Yields of trimethylene oxides are also high in those 3-chloro-1-alkanols where elimination is impossible and where steric hindrance would prevent intermolecular substitution.

Substitution of the chlorine atom of chlorohydrins by nucleophilic reagents such as the amino or substituted amino groups, mercapto groups, cyanide ion, sulfide ion, phenoxide ion and iodide ion takes place easily.

Due to the displacement of electrons toward the chlorine, the alcohol group of α chlorohydrins is less susceptible to attack by electrophilic reagents than unsubstituted alcohols. Thus, the chlorohydrins of the 2-butenes are reported to be inert to the action of fuming hydrochloric acid or zinc chloride-hydrochloric acid—nor is there any reaction with fuming hydrobromic acid. The half life of trans-2-chlorocyclohexanol with fuming HBr at 20°C is 85 days compared to a half life of 20 minutes with cyclohexanol. On the other hand 3-chloro-1-propanol where the chlorine and hydroxyl groups are further removed from each other reacts readily with 48% HBr.

The hydroxyl group of chlorohydrins, on the whole, exhibit the characteristic reactions given by simple alcohols. Oxidation of chlorohydrins containing a primary alcohol group yield chloroaldehydes and chloroacids. Halides of phosphorus replace the hydroxyl group with ease and reaction with organic acids or acid chlorides form esters.

Reaction of (+)-threo-3-chlor-2-butanol with thionyl chloride gives equal amounts of *dl*-2,3-dichlorobutanes but no meso dichloride. This stereochemical result can be accounted for by a mechanism involving the formation of the ester which subsequently decomposes to the chloronium ion due to the displacement of the negative ion SOCl^- by the neighboring chlorine atom. A nucleophilic displacement by chloride ion yields the final products.

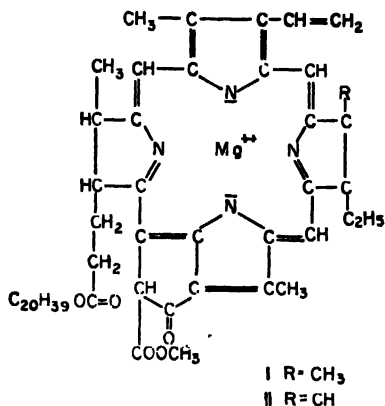
H. W. HEINE

Cross-references: Chlorine, Alcohols

CHLOROPHYLLS

A group of closely related green pigments occurring in leaves, bacteria and organisms capable

of photosynthesis. The major chlorophylls in land plants are designated *a* and *b*. Chlorophyll *c* occurs in certain marine organisms. Because of the overwhelming percentage of the total photosynthesis which is performed by marine organisms, it is possible that chlorophyll *c* is equivalent in importance to chlorophyll *b*. Chlorophyll *a* is several times as abundant as chlorophyll *b*. Bacteriochlorophyll contains two more hydrogens than the plant chlorophylls and has the vinyl group altered to an acetyl.



Formula I represents one of the canonical forms for chlorophyll *a*. II the similar form for chlorophyll *b*. These structures have been established by a long series of degradation studies mainly by R. Willstätter, Hans Fischer and their collaborators, and by synthetic studies in the laboratories of Fischer.

The biological significance of the chlorophylls stems from their role in photosynthesis, the process by which plants fix the sun's energy in the form of organic matter. This process corresponds to the reversal of the combustion of hydrogen. The oxygen liberated is set free in the air. Under special conditions, some organisms are also capable of liberating the hydrogen, but usually this is used for chemical reductions in the plant. Atmospheric carbon dioxide is fixed enzymatically and is thus used as the source of the carbon in the synthetic process but is not reduced directly. The path of the carbon from carbon dioxide in photosynthesis has been elucidated largely by the studies of Calvin and his collaborators. While it is known that most of the energy fixed in photosynthesis is absorbed originally by the chlorophylls, the exact reactions which they undergo to initiate the process of reduction are not yet understood. It is known, however, that the photosynthetic sequence requires a high degree of organization within the plant cells where it occurs, and that destruction of the organization of the chloroplasts by processes like grinding are sufficient to bring photosynthesis to a stop, even when the chlorophyll and the soluble enzymes participating in the process are still presumably intact.

Weak acids remove the magnesium from the chlorophylls giving the pheophytins. Strong acids selectively hydrolyze the phytyl group, yielding the pheophorbides. Hydrolysis of the chlorophylls

by the enzyme chlorophyllase in the absence of alcohols also removes the phytyl group, giving chlorophyllides. When the enzymatic process is conducted in the presence of alcohols, chlorophyllide esters, such as methyl or ethyl chlorophyllide, are produced by alcoholysis. The chlorophylls, because of the phytyl group, are microcrystalline waxes. The chlorophyllides, on the other hand, crystallize in visible crystals.

Hot, quick, alkaline saponification of the chlorophylls yields chlorophyllins, magnesium containing pigments with three carboxylate ions. These result from the removal of the two alcohol groups and the cleavage of the five-membered isocyclic ring. The cleavage occurs readily because this ring contains a keto group β to a carboxylic ester group. Acidification of the product obtained in this manner from chlorophyll *a* removes the magnesium and gives chlorin *a*, one of the most readily obtainable and important degradation products of chlorophyll *a*. The corresponding degradation product of chlorophyll *b* is called rhodin *g*. The numerical subscripts in this and lower ranges refer to the number of oxygen atoms contained in the molecules. In the high ranges, for example pheopurpurins, the subscript refers to the so called "acid number", the percentage strength of hydrochloric acid which will remove two-thirds of the substance from an equal amount of its ethereal solution.

When an ethereal solution of a chlorophyll, or of a derivative containing an intact isocyclic ring, is treated with cold alcoholic KOH, the green color is momentarily discharged to a yellow or brown, depending upon the derivative, and the green color then reappears. This is known as the "phase test" and was discovered by Molisch. When chlorophyll derivatives are exposed to air in the presence of alkali, oxidation accompanies the hydrolysis and ring cleavage and the product is said to be "allomerized". Such a product will no longer give a positive phase test, nor will it crystallize readily. The prevention of allomerization is of great importance in securing high quality chlorophyll derivatives. The complicated series of reactions taking place during allomerization was elucidated by the work of J. B. Conant and his collaborators. Equivalent oxidation can also be secured with quinone. Stronger oxidizing agents, such as ferricyanide or molybdicyanide, are capable of stripping off the extra hydrogens from the nucleus and converting members of the green chlorophyll series into the red porphyrins. Chromic acid degrades all these substances into maleic imide derivatives, together with other products.

Mild hydrogenation of chlorophyll derivatives saturates the vinyl group. Drastic hydrogenation is capable of discharging the color, with formation of leuco compounds, or even of cleaving the nucleus with the formation of pyrrole derivatives.

It is thus evident that the chlorophylls are sensitive to acid, alkali, reducing agents or oxidizing agents, whether weak or strong. This variety of sensitivities to chemical agents renders them hard to purify without change and makes chemical synthesis in the field difficult. In commercial practice, it complicates the problem of securing uni-

formity of product and gives rise to the possibility that each batch will contain different substances or different proportions of various products. The sensitivity of the *b* series to chemical reagents is generally greater than that of the *a* series.

Compared to the highly stable phthalocyanines, chlorophyll derivatives are pigments of relatively low stability to light, oxidizing agents and other common pigment destroyers. This property forms one of the serious limitations to their wider commercial exploitation. A moderate increase in stability is conferred by the substitution of copper for magnesium. This also produces a clearer shade that is frequently more desirable. Numerous metals which have square, planar bonds are quite tightly bound by chlorophyll derivatives. This is especially noticeable in the case of copper, which is so tightly held in this configuration that it is deprived of its usual catalytic action. Even these complexes possess relatively low stability to light and oxidizing agents, however. An additional difficulty is introduced by the fact that the destruction of the organic portion of the molecule renders the metal available for new combinations.

Commercially, chlorophyll derivatives are usually assayed spectrophotometrically or colorimetrically. These assays serve as an index of tinctorial power but do not accurately measure the chlorophyll derivatives because of the interferences of other plant pigments and decomposition products. For reliable assays, preliminary fractionations must be performed.

The special techniques most frequently used in the fractionation and purification of chlorophyll derivatives are acid fractionation, column chromatography and paper chromatography. The acid fractionation procedure of Willstätter and Mieg relies upon the fact that porphyrins, chlorins and related substances are weak bases which can be extracted from ethereal solutions by varying concentrations of hydrochloric acid. The fractionations obtained are sharper than might be expected because small changes in acid concentration cause changes in the solubility of ether in acid and of aqueous acid in ether, thus producing greater effects than they would in a relatively invariant system. The method of chromatography was invented by Tswett expressly for the separation of chlorophylls and carotinoids but lay dormant in the literature for many years until rediscovered for the fractionation of carotinoids. Paper chromatography is a powerful tool for assay because of the small quantities of material needed for a satisfactory fractionation. Even these small quantities, however, are sufficient for quantitative purposes when eluted and assayed in a spectrophotometer.

Chlorophyll derivatives with the phytol group intact are oil-soluble and form a series of green dyes which have found wide commercial application in the coloring of oils and waxes. The chlorophyll soaps, resulting from combined saponification and cleavage of the isocyclic ring, form valuable "water-soluble" dyes, useful in the coloring of soaps and similar products.

Both the medical and the cosmetic literature are replete with claims of therapeutic or physiological activity of "chlorophyll". The substances utilized

in this work range from partially purified chloroplasts to mixtures of materials which have undergone deep-seated chemical alteration. Some of the types of activity claimed can be shown to be due to incidental impurities. The field for investigation of the action of pure chemical individuals produced by the action of various reagents upon chlorophyll or its derivatives is unexplored. It is known, however, that neither chlorophyll nor hemoglobin in the diet is utilized by the body in the formation of the physiologically active pyrrole pigments. These are derived, instead, from such simple building blocks as glycine and acetate ion. Only the iron in dietary blood pigment can be utilized by the body.

The work of Granick has shown that, in the physiological processes of plants, chlorophyll is formed from protoporphyrin, which can be obtained in the laboratory by the removal of iron from hemin. The pathways to heme and to chlorophyll diverge at protoporphyrin. To form heme, an organism introduces iron into protoporphyrin. To form chlorophyll from protoporphyrin, an oxidation, a reduction, a ring closure and esterifications are performed and the magnesium is introduced. The end product of the enzymatic synthetic chain is presumably protochlorophyll, the magnesium derivative of the porphyrin corresponding in structure to chlorophyll. The addition of the two hydrogens necessary to convert the red compound to the green is accomplished under the influence of light.

A. H. CORWIN

Cross-references: *Photosynthesis*

CHROMATES, *see* CHROMIUM

CHROMATOGRAPHY

Chromatography is one of the most versatile procedures available to the chemist for the fractionation of mixtures of substances. In the operation of a chromatogram, a mobile gaseous or liquid phase is used to wash the substances to be separated through a column of a porous material. In this manner, the components of the mixture are distributed reversibly between the nonmobile and the mobile phase, and the selective forces of sorption, upon which the fractionation depends, are thus utilized in a countercurrent, multistage procedure that can possess extremely high resolving power. Michael Tswett, a Russian botanist, gave chromatography its name in 1906, and is generally credited with being its discoverer, although other investigators performed somewhat similar experiments at an even earlier date. In his experiments, Tswett poured a petroleum ether extract of green leaves over a column of finely powdered calcium carbonate contained in a vertical glass tube. The pigments in the extract were first adsorbed at the top of the column, but as more fresh solvent was percolated through the column, the individual components of the mixture began to migrate down the column as discrete zones, each at its own characteristic rate, so that in time the pigments were separated from one another. The resulting dramatic display of colors

inspired the name "chromatography", which, as it turns out, was not a particularly fortunate choice, for today the technique is used more often than not for the separation of colorless substances.

Effective separations on a chromatogram depend upon the selection of the right combination of stationary and mobile phases, a selection which, even now, must frequently be made empirically. An enormous number of finely powdered materials have been employed as the nonmobile phase in a chromatograph column, including the carbonates of calcium, magnesium, and sodium; various forms of charcoal activated in special ways; fuller's earth, bentonite, Lloyd's reagent, talc, and innumerable other clays and diatomaceous earths; alumina; silica gel; and many organic substances such as starch, cellulose, sucrose, inulin, benzoic acid, and synthetic ion exchange resins. The solvents employed as mobile liquid phase, or eluant, include water, aqueous solutions of various acids, alkalies, and salts; the lower alcohols; ketonic solvents; hydrocarbons and chlorinated hydrocarbons; various ethers and derivatives of ethylene glycol; and many others alone or in combination.

Once the components of a mixture have been separated into zones on a chromatogram, they are sometimes recovered by extruding the column, segmenting it, and extracting each segment separately to recover the adsorbed substance. More frequently, however, passage of solvent through the column is continued until the various zones emerge successively in the effluent issuing from the bottom of the column, a procedure known as elution analysis. Each zone is collected as one or more fractions. To locate and identify substances, either on segments from a column, or in the effluent fractions, numerous physical and chemical techniques have been employed, including conductivity, spectroscopy, fluorimetry, color reactions, radioactivity measurements, determinations of enzymatic activity, and bioassay with a microorganism or an animal.

In recent years, several modifications and alterations in the basic Tswett technique have been introduced. In the so called "partition chromatogram", developed by Martin and Synge, the column of porous solid is used to immobilize droplets of a liquid phase, and separations are considered to result primarily from liquid-liquid distribution of the solutes between the stationary and the flowing liquid phases. In frontal analysis, as introduced by Tiselius and Claesson, the mixture to be fractionated is not applied to the column as a discrete sample followed by fresh solvent, as in elution analysis, but a solution containing the substances to be separated is continually passed into the column of adsorbent. The concentration of solutes in the effluent rises in a stepwise fashion as each component in turn saturates the column and breaks through into the effluent. The number of steps in the effluent curve indicates the complexity of the mixture. Alternatively, when the column is nearly saturated, a very strongly adsorbed compound can be used to displace a group of substances, which then emerge in the effluent as a series of immediately adjacent zones.

Separations of gases can also be achieved chro-

matographically by allowing the mixture to flow over either a solid or a finely dispersed liquid, yielding a gas-solid or a gas liquid chromatogram.

Probably the most important recent development in chromatography was made by Martin and Synge and their associates in England when they introduced the use of strips or sheets of paper as the stationary phase in a chromatogram. The mixture to be fractionated is applied as a spot to one end of the paper, whereupon the paper is enclosed in an airtight container. The end nearest the spot dips into a reservoir of solvent, and liquid is allowed to flow over the paper by capillary action. The substances migrate at different rates and arrange themselves as spots on the paper. A wide variety of chemical tests or physical measurements can be used to locate the spots.

Paper Chromatography. Increased resolving power can be obtained if a square of paper is employed. After the chromatogram is run in one direction, the solvent is dried off and the paper then turned through a right angle and run with a second solvent. Each spot from the first chromatogram thus serves as the starting point for a second chromatogram with a different solvent. The components in the mixture are thus spread over the paper to give a two-dimensional pattern. Identification of a substance on a paper chromatogram is usually achieved by demonstrating a coincidence in the rate of travel in several solvents of the unknown and an authentic sample of the substance in question. Among the virtues of the paper chromatogram are its simplicity, and the fact that it can be done on a very small scale, frequently requiring only micrograms of material.

Chromatography has been used to fractionate many kinds of mixtures of organic and inorganic compounds, for example, organic acids and bases; steroids; hydrocarbons; amino acids, peptides, and proteins; purines and pyrimidines; carbohydrates; phenols; and inorganic anions and cations. Indeed, it seems likely that, eventually, any substance that can be brought into solution or vaporized easily will become amenable to chromatographic separations. Finally, the flexibility of the chromatographic method renders it a sensitive analytical technique on the microgram or milligram scale, and a preparative procedure on the hundred mg. or gm. scale.

WILLIAM H. STEIN

Cross-references: *Analytical Chemistry, Adsorption*

CHROMIUM AND ITS COMPOUNDS

Chromium (atomic weight 52.01; electrons in shells 2, 8, 13, 1; Group VI of Periodic Table) was discovered by L. N. Vauquelin in 1797 in the red Siberian mineral crocoisite, lead chromate. He named the element chromium because of the brilliant and diverse colors observed in most of its compounds. Two years later, the element was found in chromite or chrome iron ore [$\text{Fe}(\text{CrO}_2)_2$ or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$]. This mineral is the industrial source of chromium. High-grade ores have been mined in Turkey, Rhodesia, New Caledonia and

the Philippines; lower grade ores in the Transvaal, Cuba and India. High-grade ores should contain about 48% chromic oxide (Cr_2O_3). Modern methods have made it possible to utilize poorer ores. The U. S. normally imports 750,000 tons of chromite annually; these requirements were doubled during the War. Small amounts of the ore are mined in California and Oregon.

Chromium metal is white with a bluish tint; it is hard, brittle, does not tarnish and is rather inactive chemically. The density is 7, and the melting point above 1800°C . Dilute acids attack the metal but concentrated nitric acid renders it "passive". The pure metal is obtained by reducing the oxide (Cr_2O_3) with aluminum. Chromium ores are stockpiled by the U. S. Government for refractories, metallurgical and chemical purposes.

Chromite is made into bricks for lining high-temperature furnaces. Chromium is an essential constituent of many alloys. Ferrochrome is made by the reduction of chrome iron with carbon in the electric furnace. Alloy steels, often containing nickel, vanadium and tungsten in addition to chromium, are resistant to corrosion, and have great tensile strength and hardness. They are used for cutting tools, motor car parts, safes, armor plate, and projectiles. Stainless steel contains 11 to 13% chromium. Nonferrous alloys include "Nichrome" (nickel and chromium), used in electrical resistances, and "Stellite" (chromium, cobalt, and tungsten), used in cutlery.

The principal valences are +6 and +3. Chromous compounds (+2) are well defined but less important. As with vanadium and manganese, which resemble chromium chemically, the lower valence states are metallic (basic), forming the ions Cr^{+2} and Cr^{+3} , while the six-valent state is acidic and forms the ions CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$.

Chromates and dichromates have a valence of +6. Chromite is the raw material from which other compounds of chromium are made. Oxidation of chromium to a soluble chromate occurs when a mixture of the finely ground mineral with lime, and soda is heated on the hearth of a reverberatory furnace with full access of air. Sodium chromate (Na_2CrO_4) is extracted with water, and sulfuric acid is added to form the dichromate:



On standing, sodium sulfate crystallizes out and is removed. The solution is concentrated, and red, deliquescent crystals of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) separate on cooling. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) may be obtained from a solution of sodium dichromate and potassium chloride; it is less soluble and more expensive. Ammonium dichromate $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7]$ is made in a similar way.

Dichromates are red, and usually soluble. Alkalies convert dichromates to chromates:



and acids reverse the process. These changes do not involve oxidation or reduction; the valence of chromium is +6 in both chromates and dichromates. Chromates are usually yellow, (silver chro-

mate, Ag_2CrO_4 , is red); chromates of heavy metals are usually insoluble.

Chromium trioxide (CrO_3) is formed when potassium dichromate is treated with concentrated sulfuric acid. The red needles are extremely soluble in water. The solution, often called "chromic acid", appears to contain the ions CrO_4^{2-} , HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$. Pure chromic acid has not been obtained. A mixture of a dichromate and concentrated sulfuric acid is a powerful and corrosive oxidant; it is often used for cleaning laboratory glassware. Contact with the skin should be avoided. Chromium trioxide decomposes when heated, forming green chromic oxide [Cr_2O_3] and evolving oxygen. Ammonium dichromate acts in a similar way; when a small amount of the solid compound is heated at one point in the mass, the reaction is self-sustaining and the red dichromate is changed to a voluminous mass of green chromic oxide. In this case, nitrogen is evolved.

Chromylchloride [CrO_2Cl_2] a derivative of the trioxide, is formed by heating a mixture of a dichromate, a chloride (NaCl), and concentrated sulfuric acid. Red vapors distill off, which condense to a red liquid. This reaction serves to distinguish chlorides from bromides and iodides, which do not form chromyl compounds. Severe explosions of chromyl chloride have been reported. Solutions of chromates and dichromates are toxic, and dust from such compounds may constitute an industrial hazard.

There are many uses of sodium and potassium chromate and dichromate, including the tanning of leather, as a mordant for textiles, the pickling of metals, a preservative for wood, the manufacture of dyes and intermediates, a powerful oxidant in analytical chemistry and in organic syntheses, and in the manufacture of pigments. Chrome Yellow is lead chromate, Chrome Red, a basic chromate of lead, and Zinc Yellow, a basic chromate of zinc, used in corrosion inhibiting paints for steelwork on ships, and light alloys for aircraft.

Chromic compounds have a valence of +3, and are colored violet or green. A number of chromic salts have been prepared in two or more forms (1) violet salts which contain the ion Cr^{+3} or $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$, and green compounds in which part or all the chromium is present as a complex ion. In some cases, two or more green modifications have been reported.

Chromic sulfate [$\text{Cr}_2(\text{SO}_4)_3$] is formed by the reduction of a dichromate by sulfur dioxide in the presence of sulfuric acid. It combines with potassium sulfate to form chrome alum, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ or $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. In industry, large amounts of chrome alum are obtained as a by-product in the oxidation of anthracene to anthraquinone by potassium dichromate. A solution of chrome alum in cold water is violet; if heated to 70°C . it becomes green. Chrome alum is used as a mordant, and in tanning leather.

Chromic hydroxide [$\text{Cr}(\text{OH})_3$], a grayish green, gelatinous substance, is precipitated by alkalies from solutions of chromic salts. It dissolves in an excess of sodium hydroxide, forming a green solution, probably containing a chromite, NaCrO_2 .

Green *chromic oxide* (Cr_2O_3) is made by heating the hydroxide, or ammonium dichromate. It is used as a catalyst and is an excellent but rather costly pigment.

Chromic chloride (CrCl_3), violet plates, is obtained when chlorine is passed over a heated mixture of chromic oxide and carbon. It is insoluble in water but dissolves readily if a trace of chromous chloride (CrCl_2) is added. A violet and several green forms are known.

Chromous compounds have valence +2. When a red solution of a dichromate is reduced by zinc and hydrochloric acid in an atmosphere of hydrogen, the color changes to green (CrCl_3), and finally to intense blue. The blue solution contains chromous chloride (CrCl_2). Chromous salts find some applications in chemistry as extremely powerful reducing agents. They oxidize spontaneously to chromic salts upon contact with air.

Chromium is a constituent of many interesting compounds, which have, as yet, no industrial uses.

Chromium hexacarbonyl [$\text{Cr}(\text{CO})_6$], a stable, white solid, is formed when a suspension of chromic chloride in an ethereal solution of the Grignard Reagent ($\text{MgC}_2\text{H}_5\text{Br}$) is acted on by carbon monoxide under pressure. It is purified by distillation. The shape of the molecule is octahedral.

Hein prepared a remarkable series of organochromium compounds, containing three, four and five phenyl groups. The formulas reported, such as $(\text{C}_6\text{H}_5)_3\text{CrOH}$, tetraphenyl chromium hydroxide, indicated the unusual valence of five for chromium. All of the compounds are red.

Chromium, like cobalt and platinum, is the central atom of a large number of coordination compounds. The coordination number is six, and the shape of the complexes is octahedral. The chromium amines, such as $(\text{Cr}(\text{NH}_2)_6)\text{Cl}_3$, closely resemble the corresponding compounds of cobalt, even in color. Werner obtained optically active isomers from the *cis*-ethylenediamine salt [$(\text{CrCl}_2\text{en}_2)\text{Cl}$] as well as from the trioxalatochromate(III) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$, a final proof of the octahedral configuration. Chromium also forms many coordination compounds containing cyanogen and thiocyanate groups. Reinecke's salt [$(\text{NH}_4)_2(\text{Cr}(\text{NH}_2)_2(\text{CNS})_4)$], used in biological chemistry, belongs to this class.

Detection and Estimation. Chromium compounds produce an emerald green color in the borax bead, when heated in the reducing flame. If a chromium compound is fused with solid potassium hydroxide and nitrate, a yellow chromate results.

If hydrogen peroxide is added to a solution of a dichromate containing a little sulfuric acid, and the mixture then shaken up with a small amount of ether, a blue ethereal layer is formed above the aqueous solution. The blue color is due to the formation of a perchromate, probably CrO_5 . Several series of perchromates have been reported, one red in color. The valence of chromium is probably 6 in these compounds.

Chromium may be estimated quantitatively in chromic salts by precipitating the hydroxide with ammonia, and igniting to the oxide.

The estimation of chromium in chromates and dichromates is usually effected by volumetric methods. These usually depend on the oxidation of ferrous salts or the liberation of iodine from potassium iodide.

T. P. McCUTCHEON

CLARIFICATION

Clarification is one of many processes used to separate solids from liquids. It is an unusually important industrial operation involving gravitational settling of suspended solids and the removal of a more or less clear, liquid portion. The application of this process is particularly desirable when the quantity of material to be treated is quite large and perhaps too great to handle by ordinary filtration methods.

The settling rate of particles suspended in a liquid under the influence of gravity is governed by many factors, namely the physical properties of the solid phase and the liquid medium, the density of the suspension, and the presence of flocculating forces peculiar to the pulp in question. During the initial stages of settlement at high dilution ratios of liquid to solids, the terminal settling velocities of all the particles are practically constant and can be determined by Stokes' formula:

$$u_t = \frac{g_L D_p^2 (\rho_s - \rho)}{18\mu}$$

where g_L = local acceleration due to gravity, ft/(sec.)²

D_p = diameter of particle, ft.

ρ_s = true density of particle, lb. mass/ft.³

ρ = fluid density, lb. mass/ft.³

μ = fluid viscosity, lb. mass/(ft.) (sec.)

u_t = terminal settling velocity of particle under action of gravity, ft./sec.

However, a condition may soon be reached when the falling particles exert a mutual interference and the particles then tend to settle collectively at a reduced velocity. A pulp concentration is finally achieved after which the settling rate is greatly retarded. This point of sedimentation is usually regarded as separating the initial "clarification" and the final "thickening" zones. In the thickening zone, much of the water is eliminated through consolidation and compression by virtue of the overhead weight of other particles. Commercially, the dewatering efficiency in this stage is greatly improved by a gentle stirring action of rakes which changes the random arrangement of particles and results in a greater degree of compaction.

The above principles of sedimentation have been utilized for centuries in many different ways. The original methods of clarification or thickening involved the use of flat-bottomed settling tanks operated on a batchwise basis. These tanks would be filled with dilute pulp and the solids permitted to settle for the required period of time, after which the supernatant liquor was removed by decantation and the settled sludge manually dis-

charged by shoveling. This procedure would usually be periodically performed in a multiple number of units so that a continuous supply of processed material could be maintained.

Somewhat later attempts were made to develop continuous methods of thickening. Some success was achieved by the use of cone-bottomed tanks to which the feed was admitted continuously. The clarified liquor was continuously overflowed at the top and the underflow of thickened sludge discharged through an opening at the bottom. The main disadvantages of this system were (1) build-up of solids on the walls of the equipment, (2) size limitations and multiplicity of units required for large-scale operations, (3) nonuniform density of underflow product, and (4) excessive labor requirements to assure good operation.

The greatly improved devices for thickening now available are very similar in that they consist of a large shallow settling tank, an overflow for the clarified liquor, and most important, a suitable mechanism for the positive removal of the thick underflow sludge. The Dorr, Denver, and Hardinge thickeners are among the several principal makes currently marketed; and the major difference between the various units is associated with the type of mechanism employed to discharge the settled solids. For this purpose, movable rakes, plows, drags, and internal scrolls have been used in different forms and arrangements.

In the operation of the usual thickener, the feed is continuously introduced at the surface near the center or the rim of the tank and in such a way as to avoid undue turbulence. The solids which settle to the bottom are slowly raked toward a center discharge opening by means of the revolving mechanism. The liquid, colloidal material, and any unsettled solids overflow continuously into a collection channel over the whole periphery or segment thereof, depending on the method of feeding employed. Mechanical continuous thickeners have been built in sizes ranging up to 325 feet in diameter. For cases where the availability of floor area is limited multi-compartment units with as many as five compartments are also obtainable.

Thickeners are employed in numerous metallurgical and chemical process applications, e.g. as well in the production of fertilizers, beet sugar, cement, magnesia, alum, and many other products. They are also employed for thickening flotation concentrates, for recovering fine coal in coal washing plants, for water softening and sewage purification.

WALTER C. LAPPLE

Cross-references: *Colloid Chemistry, Filtration*

CLASSIFICATION

This term refers to separation of particles of various sizes by mechanical means, including screens, settling tanks, clarifiers, etc. The products of many chemical reactions involving solid materials may be seriously damaged in quality and appreciably lowered in yield if the reaction does not go to completion, or if the products and

reactants are allowed to remain in contact after the primary reaction has been completed and undesired secondary reactions are permitted to occur. Consequently, for many reactions, it is necessary that all particles be of similar size so that reactions can go to completion with a minimum production of unreacted cores and of products of side or secondary reactions.

Very fine particles of a material may also have deleterious effects in a reaction mass other than directly harming the quality of the product. They may consume reacting chemicals without producing any usable end products. The presence of the fines may create difficulties in circulating reacting liquids or gases through the solids. They may be difficult to remove from products or otherwise complicate operations of purification after the reaction is completed.

The most accurate method of sizing solids is by separating them on the basis of their cross-section, thickness, diameter or other dimension. The separation is carried out by removing that material which will go through an opening of a set size from that which will not.

A second technique for size classification is based on the fact that a large particle of the same density as a small one has less exposed surface per unit of weight and will therefore be less affected by its surface as it passes through a gaseous or liquid medium. Put more simply, a large particle will settle more rapidly if dropped in a fluid (gas or liquid); it will travel farther horizontally in a fluid if given an equal initial horizontal velocity; it will be lifted with greater difficulty, and carried a shorter distance by a stream of fluid and dropped more quickly if the fluid stream is suddenly reduced in velocity; or if acted upon by centrifugal force while suspended in a fluid, it will be thrown out of the fluid with greater ease than will the smaller particle.

A third technique is based on the fact that a large particle is less impeded in its travel down an inclined roughened surface than is a small particle.

Although solid materials in the form of a continuous filament such as thread or a continuous sheet such as paper is graded on the basis of actual thickness, the normal conception of classification by dimension is an operation known as screening, a technique particularly adaptable to disintegrated solids.

Screening equipment is manufactured by a number of firms. Since each attempts to meet competition, it is not surprising that there is such a large variety of screens available. As major divisions, there are rotary screens and flat screens; the latter may be vertical, inclined, or horizontal, and may be stationary, traveling, shaking, or vibrating. Screens may be arranged to operate on dry materials or on materials suspended in a liquid.

Screens have two major parts: the screen surface, and the mechanisms for presenting fresh material to the screen surface and for moving the oversize off the screen. Auxiliaries, such as positive means of moving material through the screens, and devices to dislodge blinding particles, reduce

dusting, regulate feed, and remove products are often provided.

Solid material, fine enough to be floated or carried by a stream of gas or liquid but still heavy enough to settle if allowed to remain in a quiescent state, presents good possibilities for separation into size ranges. Moreover, separations which make use of this property often can be accomplished at a fraction of the cost of the screening operations. The accuracy of separation is sometimes not as good as that obtained with the screen, but with the latest improvements, claims are made for accuracies which are quite remarkable.

The technique of selective settling from a quiescent medium is usually limited, on a practical scale at least, to settling solids out of liquid media. In this technique the solid mixture, suspended in a stream of the liquid, is directed by the stream into some type of equipment which has a reasonably large volume and in which the speed of liquid flow is greatly reduced. The heavier solid particles are settled out, while the lighter ones leave with the liquid in the overflow.

Classifiers, decanters, or thickeners serve as equipment for this purpose. All provide a settling basin, an overflow for the water carrying the finer particles, and some means for removing the heavier particles which settle out.

If slight or sometimes quite energetic agitation is given the suspending media, the settling of finer particles may be hindered to such an extent that heavier particles will pass through the suspension and will be deposited in layers roughly indicative of their size. Several operations have been developed using this principle. None are presently of any particular commercial importance.

If solid material is held in suspension in either a gas or a liquid, and if the suspension is caused to rotate rapidly around a guide, the solid material will be thrown out by centrifugal force; the finer or lighter the particle, the faster the rotation must be to effect removal by this means. Consequently, by changing the diameter of the unit, or the velocity of stream flow, size separation can be obtained.

Air separation is most important, and there are many makes of such equipment. These units all have the same basic design and vary only in detail. In some types the motion of the gas through the unit is induced entirely by introducing the air at high speed tangentially into a cylindrical or conical chamber; in the others the speed of the air is created by a centrifugal fan located in the separator in such a fashion as to whirl the gas within the separation chamber.

The principle that a large particle will be less influenced by a roughened surface over which it rolls than will a small one of the same density is the basis for several separation techniques. The methods in use are given the general descriptive name of "tabling". The separation can be carried out on a wet table, a dry table, or in a so-called "spiral concentrator".

B. E. LAUER

CLATHRATE COMPOUNDS

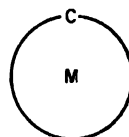
In 1886 Mylius made careful observations on complex compounds formed by quinol with certain volatile compounds, such as hydrogen sulfide, sulfur dioxide, and hydrogen chloride. He found these compounds to contain three or four molecules of quinol to each molecule of the other component. He suggested that no ordinary combination occurred between the two types of compounds but that during crystallization the quinol molecules were in some way able to lock the volatile compounds into position without chemical bonding. It seemed probable that the compounds resulted from the complete enclosure of one molecule by two or more molecules of another component, in such a manner as to prevent escape unless the strong forces which bound together the enclosing molecules were broken.

Palin and Powell verified this work. They found that the quinol molecules link together through hydrogen bonds to form infinite three-dimensional complexes of trigonal symmetry and that these giant molecules may enclose a second component. Powell observed the firmness with which they were held together though their components appeared to have no strong attractive forces between them. He observed that they were held by the enclosure of one by the other, of both by each other, or by some other uncommon mechanism. Because of this unusual type of binding he proposed that they be called "clathrate" compounds, from the Latin word *clathratus* meaning enclosed or protected by cross bars of a grating.

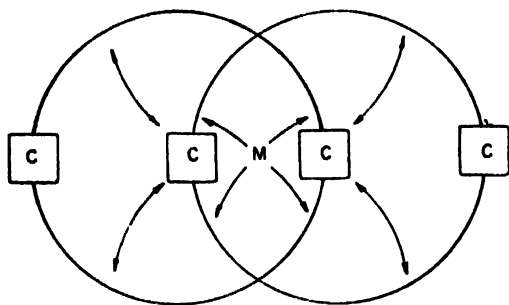
It has been observed that size and type of bonding within the cage-like portion of the molecule are important factors. The spaces must be bounded to prevent escape of the enclosed molecules and the molecule to be enclosed must be properly oriented when the cage is closing. In certain types of dissociation reactions molecules have been observed to escape from within the "cages".

In general the preparation of clathrate compounds is quite simple. Many have been prepared merely by crystallization from a medium composed of the molecules to be enclosed. The resulting crystals are stable under ordinary conditions but decompose when heated near their melting points, when dissolved in water or when ground in a mortar.

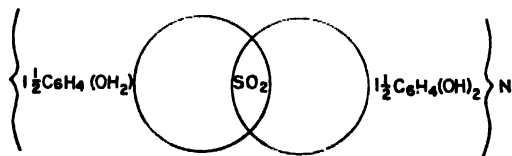
To explain the structure of these compounds Powell introduced the encirclement formula. Such formulas may be used where C gives the composition of the cage and M that of the enclosed compound. The formula,



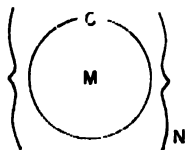
shows a simple clathrate molecule. The formula,



indicates an infinitely extended complex in a crystal. The formula of any clathrate compound is determined by the ratio of available cavities to the amount of cage material. To illustrate, the encirclement formula for the compound $3\text{C}_6\text{H}_4(\text{OH})_2 \cdot \text{SO}_2$, may be written:

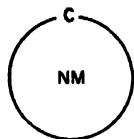


The interlocked rings denote mutual enclosure of two identical cageworks. The subscript N outside the brackets shows that the cages are infinitely extended and that there is multiple enclosure of each cagework by the other. The resulting unoccupied space is filled by the inorganic molecule, SO_2 . Powell employed the following diagram to explain the restrictions of the SO_2 molecule within the cage:



According to this representation the enclosed molecule, M, could escape by pushing apart the two independent portions of its cage, against their van der Waals attraction. Although this may be a large force, nevertheless if an attempt is made to enlarge the holes of exit the cages will necessarily be brought together more closely elsewhere. Larger repulsion forces will result and prevent enlargements of the exits. The effectiveness of these forces is contingent upon the stability of both the H-bonds and the covalent linkages.

The general encirclement formula,



may be applied to all clathrate compounds. In the formula NM there may be:

(1) A whole number, N, of molecules of component M.

(2) Any fractional amounts of two or more enclosed molecules that add up to a whole number.

(3) Fractional amounts, as in (2), with the qualification that one of the enclosed molecules must be present in some minimum proportions needed to trap the other enclosed components.

(4) Fractional amounts that do not add up to a whole number. This situation may occur when some of the cavities are unoccupied.

Volume alone, not chemical nature, determines the type of molecule, M, to be enclosed. The lower and upper limits of the size of M are governed by the size of the cavities and the sizes of the available exits in the framework. Physical methods are used to make the final decisions in assigning compounds to the clathrate group. However, preliminary assignments may be made as a result of investigations as to properties, molecular ratios, relative volumes of components, and the behavior of homologous or related substances.

SISTER MARY MARTINETTE

CLAYS

In general the term "clay" implies a natural earthy, fine-grained material which develops plasticity when mixed with a limited amount of water. By plasticity is meant the property of the moistened material to be deformed under the application of pressure, the deformed shape being retained when the deforming pressure is removed. Chemical analyses of clays show them to be essentially silica, alumina and water, frequently with appreciable quantities of iron, alkalis and alkaline earths. The term "clay" has no genetic significance, but is used for material that is the product of weathering, has formed by hydrothermal action, or has been deposited as a sediment. As a particle size term, the clay fraction is the one composed of the smallest particles.

Quantitative chemical analysis alone does not explain either the differences in properties some of the clays exhibit, although their composition as found by analysis is the same, or why some clays have similar properties although they differ in chemical composition. Some of the reactions, like gelation, led to the assumption that clays represent matter in the amorphous state. The introduction of two new research tools, the x-ray diffraction technique and the electron microscope, demonstrated that clays have a crystalline structure. The great variations in properties can be accounted for only by assuming that the clay minerals are composed of comparatively simple building units, and that the differences are primarily due to the manner in which these units are put together.

The "mortar" used in the building of the clay minerals is the unsaturation of their ultimate building units. For example, a silicon atom will share four electrons with a neighboring atom ($\text{Si} = +4$). An oxygen atom needs two electrons for saturation ($\text{O} = -2$). Therefore, the silicon-oxygen tetrahedron (SiO_4) is not saturated. If several of these tetrahedra combine by sharing oxygen atoms, a chain like structure results. In

such a chain, two of the oxygen atoms belonging to every silicon atom remain unsaturated. This deficiency can be compensated for by adsorbing, for example, sodium ions. This will result in a fibrillar aggregate known as *sodium silicate* or *water glass*. The fibrous structure and the high degree of hydration of the sodium ion explain the high viscosity exhibited by solutions of water glass.

The electrical forces associated with a colloidal particle in an electrolytic medium arise from two sources. One set of forces arises from the ions which are rigidly bound to the surface of the particle, and the other is due to the ions of opposite sign which concentrate around the particle in an effort to neutralize its charge. Inasmuch as the particle still carries a net charge, the number of counter ions must be insufficient for neutralization. Since some ions of opposite sign are randomly floating in the dispersion medium, it will carry a charge opposite to that of the colloidal micelle.

Owing to the adsorption of ions from the dispersion medium by the colloidal particle or to the dissociation of ions from its surface into the dispersion medium, as is typical for clays of the bentonite group, the dispersion medium will possess an excess of ions of a charge opposite to that of the particles. This is evidenced by the phenomenon known as the *electroviscous effect*, which is due to a drag caused by the dispersion medium carrying the counter charges moving toward one pole and the dispersed particles moving to the other pole in an electric field. This electric field, if of sufficient strength, can cause condensation and orientation of the colloidal micelles. This condition will exist until the attraction forces resulting from the charge on the particles and the ions in the dispersion medium are in balance with the forces of repulsion between the ions in the adsorbed diffuse layer and those freely moving in the dispersion medium. Thus, a thixotropic gel will form, but it will immediately revert to a sol if the free movable ions are redistributed, for example by agitation. If the concentration, valency, or hydration of the counter ions are such that the magnitude of the net charge of the colloidal micelle or the thickness of the diffuse double layer is so reduced that van der Waals' attraction forces come into play, coagulation will result.

The most important and interesting phenomenon exhibited by those clay minerals which will form a colloidal micelle upon contact with water is the ion-exchange reaction. This reaction was originally recognized by Thompson in his investigations of the properties of soils; the first systematic work on it was done by Way.

As has been shown, the ultimate clay crystal carries a net negative charge. This charge results from anion adsorption onto the surface or from an unbalanced crystal lattice. The clay particle is a very complex anion. Therefore, to balance its charge, the particle will have the tendency to adsorb the necessary number of cations available in its environment. When such a clay particle is then redispersed in water, these cations will hydrate and, depending on their valency and degree of hydratability, will dissociate to a certain dis-

tance from the surface of the particle and thereby build up a diffuse electric double layer and give rise to the formation of a colloidal micelle. Therefore, one may compare the suspended clay particle with a dissociated electrolyte, the size of one of its ions falling within the colloidal range of dimensions. A similar condition exists in the case of soap, where the sodium ion, owing to its hydration, will dissociate from the fatty acid ion when the soap is brought into contact with soft water. If hard water is used, however, then the divalent and less hydrated calcium ions contained therein will exchange for the sodium ions and form the far less soluble calcium soap.

By the same mechanism the so-called counter ions belonging to the clay particle may also exchange with ions present in the dispersion medium if these ions have a higher valency and therefore have less tendency to carry adsorbed water molecules with them. The magnitude of this ability to adsorb cations depends on the structural configuration of the nucleus of the colloidal clay micelle. It is expressed in milliequivalents of cations per 100 grams of clay. Below are given the exchange capacities of the most important clay minerals.

Mineral	Base-Exchange Capacity (meq./100 g. of clay)
Montmorillonite	60-100
Attapulgite	25-30
Illite	20-4
Kaolinite	3-15

Ion exchange reactions of clays are important in explaining such phenomena as plasticity, dry strength, thixotropy, dilatancy, and many other properties characteristic of the clay minerals.

In the formation of bentonite particles, fractures parallel to the *c*-axis seldom take place. On these surfaces a diffuse double layer can theoretically be formed, that is, first a layer of preferentially adsorbed hydroxyl ions and then the counter ions in a diffuse arrangement. The presence of hydrogen as the counter ion, all other factors being constant, would give the greatest attraction force at the edge of the water hull, and therefore the greatest plasticity. The least plasticity should be exhibited when sodium ions serve as counter charges for the preferentially adsorbed hydroxyl groups.

Dilatancy has so far been observed only with hydrophobic suspensions, and the lower the stability of the dispersion the more pronounced the phenomenon becomes. Furthermore, only such systems have exhibited dilatancy whose particle size is not smaller than the upper limit of the colloidal range of dimensions.

Clay dispersions exhibiting thixotropy are characterized by such a distribution of ions in their diffuse double layer, resulting either from adsorption by added electrolytes or from surface dissociation, that the particles with their solvated hulls will take on equilibrium positions if left undisturbed. However, if disturbed, the solvated hulls are disrupted and the particles can then move around freely. This concept is substantiated by

the sudden change in light transmission when a bentonite sol sets to a gel, and is also in line with Langmuir's mathematical treatment of thixotropic systems, which concludes that the particles in the gel are placed like ions in a crystal and lie at considerable distance (up to 5000 Å.) from each other. They are locked into place by the balance of far-reaching attraction forces and appropriate repulsion forces set up by the interplay of the surface ions of the clay crystal and the free ions in the dispersion medium.

The phenomenon of rheopexy has so far been observed only with a few systems which are known to be thixotropic. Fine-particle-size fractions of Na-bentonite exhibit this property. Whereas the setting up of a thixotropic gel does not call for any preferential alignment of the dispersed particles, ultramicroscopic studies of rheopeptic systems indicate that the rhythmic motion applied to the sol orients and aligns the platy particles and thereby accelerates their taking up the equilibrium positions.

The phenomenon of stream double refraction may also be demonstrated by using a monodisperse Na-bentonite sol of about 1 per cent concentration. Such a sol is quite clear to the eye, has practically the same viscosity and surface tension as water, and exhibits pronounced birefringence even at very low rates of flow.

Industrial Applications. Of all the industries in which clay minerals are of importance, the ceramic industry is of course predominant. It is the property of plasticity, so characteristic of clays, which permits their being formed to practically any desired shape. However, not all clays exhibit this property to the same degree, and therefore pottery was for centuries an art which had to rely on trial and error tests before the suitability of a clay or mixtures of different clays could be established. With the comparatively recent development of the concept of the clay particle as a colloidal micelle, it has not only been possible to offer a better understanding of such properties as plasticity, dry strength, shrinkage and others, but it has also been clearly shown that the change of ceramics from an art to a science is at hand.

Since clay is one of the fundamentally most important substances in soils, it is understandable that more attention is now being paid to clay research in connection with agriculture than ever before. The clay content and the type of clay present in the soil control above all its moisture content, its ability to supply water, its acidity, its tilth, and its general properties.

The ion-exchange reaction of clay minerals has also become of importance in the domain of construction engineering. The application of this colloidal phenomenon for the reduction of soil permeability or seepage is so far the most striking evidence for the value these new concepts have in fields where the application of chemistry was unknown only a short time ago.

As far as drilling muds are concerned, a sodium-bentonite clay is introduced into the used water to obtain a thixotropic system. The purpose of the mud is to hold the rock fragments obtained

during the drilling of an oil well in suspension if the drill is at rest so that they do not sediment and form a cake around the drill and shaft. However, when the drill works it should find a minimum of resistance, and the liquid carrying the rock fragments or sand should have a low viscosity, so that it can be easily removed from the bore hole by pumping. A dispersion of clay whose repulsive and attractive forces have been so adjusted that a thixotropic system is created fulfills these requirements.

One of the most interesting and recent discoveries in the field of the applied colloid chemistry of clays is their use in the production of coherent, self-supporting, flexible films and their applicability as the basic material for moldable plastics. These films have been termed "Alsilfilm" (aluminum silicate films).

ERNST A. HAUSER

Cross-references: *Colloid Chemistry*

COACERVATION

The term "coacervation" was first used by H. R. Kruyt and H. G. Bungenberg de Jong in 1929 to describe the partial miscibility of optically isotropic liquids in which at least one of the liquids is macromolecular or colloidal in nature. The macromolecular or colloidal equilibrium liquids are known as coacervates.

If a solution of sodium sulfate is added to a warm gelatin solution, the gelatin solution can be made to contract so that it no longer fills the entire volume occupied by the water and sodium sulfate. Droplets of more concentrated gelatin solution first separate. On standing, these coalesce to form a separate liquid layer of the more concentrated gelatin solution. A warm solution of gelatin and gum arabic, in which each constituent has a concentration of about 10%, forms a single-phase solution at pH 4.5. If this solution is diluted, the gelatin-gum arabic solution can be caused to contract and two liquid phases form. Starting with the same 10% mixed solutions of gelatin and gum arabic, two liquid layers also form if the system is concentrated. One of the layers is rich in gelatin and the other rich in gum arabic. Both liquids are coacervates. If chloroform is added to a 3% solution of cellulose diacetate in certain alcohol-chloroform mixed solvents, a more concentrated solution of cellulose acetate can be caused to separate.

These are examples of coacervation. The phenomena are of very wide occurrence and apply to many macromolecular solutions. They give rise to dispersed systems in which, in a certain sense, the dispersed phase is the same as the continuous phase such as water in water. More specifically, the same continuous liquid phase exists throughout two immiscible liquids, the discontinuity between the phases being caused by an expanded liquid such as gelatin.

To define an expanded liquid will clarify the nature of the coacervation process and the physical differences underlying liquid immiscibility

involving coacervates and liquid immiscibility involving ordinary liquids.

In many ordinary solutions, the solute or dissolved material is considered to be present in a gas-like state. Among macromolecular materials, the so called solute, such as gelatin in the above examples, can be present in a liquid-like state even at very low concentrations.

The liquid state is chiefly characterized by cohesion or continuity and flow, while the gaseous state does not have cohesion or continuity but does flow. A gas tends to fill the entire space available. A liquid has a limited volume and tends to take the shape of the container. Gases are miscible in all proportions while liquids can exhibit partial miscibility.

The chain-like or randomly kinked nature of many macromolecular materials permits them to form a continuous network throughout the solution. The forces between the molecules or particles of the polymer are continually shifting, but at any instant the continuity or cohesion characteristic of the liquid state is holding the polymer network together. The network is expanded and the voids are filled with water or solvent. This is what is meant by the "solute" being present in an expanded liquid state.

In the first example cited above the gelatin solute at first fills the entire space available, i.e., the entire volume of the solvent. On addition of sodium sulfate the gelatin solution contracts and no longer fills the entire volume of the solvent. Such contraction is characteristic of the liquid-like nature of the solute. If the solute were in a gas-like state, it could not contract but would continue to fill the entire space available. Since, however, the gelatin is an expanded liquid and the voids are filled with water, water in the liquid state is common to both liquid layers.

In the case of ordinary liquid immiscibility the two liquid layers do not have a liquid that is common to both layers. There are no expanded liquids involved. Solutes, if present, are in a gas-like not a liquid-like state.

Coacervation might therefore, be defined as partial miscibility of optically isotropic liquids in which at least one of the liquids consists of two constituents both of which are in the liquid state. Since macromolecular materials tend to fulfill the above requirements better than low molecular weight materials, the commonly accepted definition first cited may be accepted until more accurate criteria for determining if a solute is present in a gas like or liquid-like form are available. It has been suggested that such differences may ultimately be differentiated thermodynamically in terms of entropy and interaction.

The coacervate state is only one, albeit a very important one, of several equilibrium states of colloid systems. It is of extreme importance in biological phenomena and doubtless will find many industrial and commercial applications as the phenomena become better known.

B. K. GREEN

Cross-references: *Colloid Chemistry; Gels; Gums, Natural*

COAL AND COKE

Coal is a solid, combustible carboniferous substance formed by the decomposition of vegetable matter without free access of air. The plant debris from which coal had its origin accumulated in peat swamps and, in the presence of stagnant water and buried under rapidly increasing deposits of vegetable matter, was decomposed in almost complete absence of air. Assisted by microorganisms, a chemical transformation took place resulting in the formation of peat. The conversion of peat into coal occurred after the disappearance of most of the water and under conditions of increased pressure and temperature. This conversion, extending over many millions of years, was progressive, leading first to lignite and then to higher rank coals, such as bituminous coal and anthracite.

Nearly all coals are of the common banded type, so called because visual inspection shows alternating layers of different color or luster. The standard ASTM classification of coals of this type by rank depends on the fixed carbon (obtained by proximate analysis) and the heating value of each coal, as shown below.

Rank	Fixed carbon (%) (dry, mineral matter free)	Heating Value (Btu./lb.) (moist, mineral-matter-free)
Meta-anthracite	98 or more	—
Anthracite	92-97.9	—
Semianthracite	86-91.9	—
Low-volatile bituminous	78-85.9	—
Medium volatile bituminous	69-77.9	—
High-volatile A bituminous	Less than 69	14,000 or more
High-volatile B bituminous	Less than 69	13,000-13,999
High-volatile C bituminous*	Less than 69	11,000-12,999
Subbituminous A coal*	Less than 69	11,000-12,999
Subbituminous B coal	Less than 69	9,500-10,999
Subbituminous C coal	Less than 69	8,300-9,499
Lignite	Less than 69	Less than 8,300

* High-volatile C coal must be either agglomerating or non-weathering (ASTM methods); if neither, coal is classified subbituminous A.

In color, lignite may be brown but all coals of higher rank are black. The usual range of specific gravity is from 1.15 to 1.5, with 1.3 a typical figure for bituminous coal. When heated out of contact with air, decomposition begins at 300-400°C, and gas and usually tar are evolved. Chemically, coal is composed chiefly of condensed, aromatic ring structures of high molecular weight. Detailed, standard methods for the analysis and testing of coal and coke have been published by ASTM.

	Anthracite	High volatile A Bituminous Coal	Lignite
Proximate analysis, %			
Moisture	4.4	1.8	36.3
Volatile matter	3.4	33.0	26.2
Fixed carbon	83.1	58.2	31.7
Ash	9.1	7.0	5.8
Ultimate analysis, %			
Hydrogen	2.4	5.1	6.8
Carbon	81.7	77.7	42.2
Oxygen	5.2	7.5	43.9
Nitrogen	0.9	1.5	0.6
Sulfur	0.7	1.2	0.7
Heating value, btu/lb.	12,810	13,920	7,140

Coal is widely distributed throughout the world, although relatively small reserves have been found in Africa, South America, and Oceania. Of the more than 7 trillion tons estimated world reserves of coal, approximately 3 trillion tons are in the United States, and large tonnages are known to be present in certain parts of Asia and Europe. In general, anthracite and the high rank bituminous coals underlie the Eastern part of the United States, while the lower rank bituminous and sub-bituminous coals and lignite are found in the West.

The majority of coal in the United States is produced from underground mines, usually by undercutting the seam of coal and then "shooting" down by explosives. Recently a minor but substantial portion of coal has been produced by "strip mining" from the surface. In the United States coal mining has become highly mechanized during recent years. Partly as a result of this, production in underground mines has averaged about 6 tons of coal per man-day, as compared to about 1 ton per man-day in other parts of the world. After the "run-of-mine" coal has been brought to the surface, it is usually screened into various sizes, and is then often cleaned by a process based on differences in specific gravity, in order to reduce the ash and sulfur content.

The United States, with about one-third of the total production, is the world's largest producer of coal. Statistics for a recent year are summarized below (U. S. Bureau of Mines):

	Bituminous	Anthracite
Production, million tons	467	41
Percent from strip mines	23	27
Value at mine, per ton	\$4.90	\$9.81

Due to increasing efficiency of fuel utilization, as well as growing competition of other fuels, production of coal in the United States has shown almost no increasing trend over the last few decades.

Approximately 80% of the bituminous coal and substantially all of the anthracite in the United States are burned to furnish power and heat. The remaining 20% of the bituminous coal is processed in coke ovens to make coke and, usually, coal chemicals.

USE-PATTERN OF BITUMINOUS COAL (U. S.)

Electric utilities	20%
Coke ovens	20%
Railroads	10%
Other industries	25%
House heating	15%
Export	10%

The use of coal for generation of electricity has increased substantially, despite the fact that increased efficiency in utilization has decreased the average consumption of coal from 3.20 lb. per kwh in 1919 to 1.10 lb. in 1952. Some other uses, particularly by railroads, have been adversely affected by competitive fuels.

In Europe, coal has been commercially processed for many years by (a) hydrogenation, to make synthetic liquid fuel, and (b) by complete gasification with steam, using the "synthesis gas" so produced to make synthetic liquid fuel, ammonia, or other chemicals. In the United States similar processes, including hydrogenation of coal to produce aromatic chemicals, are in the development stage.

Coal Carbonization. Carbonization is the process of heating coal to relatively high temperatures out of contact with air in coke ovens or other equipment. Thermal decomposition of the large molecules of the coal substance results in the evolution of volatile compounds in the forms of gas, tar and water vapors, and the formation of a carbonaceous residue of coke. Commercial coal carbonization today is confined almost entirely to the high-temperature process (900-1150°C) in batteries of chemical-recovery coke ovens. Coal (about 16 tons in each oven) is heated for about 16 hours, during which period the gas and vapors leave the oven chamber to be separated into the various coal chemicals and other products. At the end of the coking period the red-hot coke is "pushed" out of the oven and is quenched by a water spray. Most of the bituminous coals have the property of forming coherent coke on heating, and can usually be used in the process, but all other ranks of coal are unsuitable. In contrast to chemical-recovery ovens, "beehive" coke ovens produce only coke, since all the gases and vapors are burned. Comparatively few of these beehive ovens remain in operation today. Another process of relatively minor commercial interest, at least at the present time, is low-temperature carbonization (500-750°C), which yields products differing considerably in character and amount from those produced at higher temperatures.

In 1952, 90,700,000 tons of coal were carbonized in chemical-recovery coke ovens in the United States, leading to the following average quantity of products per ton of coal (U. S. Bureau of Mines):

Coke	0.702 ton
Coke breeze	0.051 ton
Tar	7.74 gal.
Ammonium sulfate	19.92 lb.
Gas	10,150 cu. ft.
Light oil	2.79 gal.

In addition, 6,900,000 tons of coal were carbonized in beehive ovens, with an average yield of 0.637 ton of coke per ton of coal. Total production of coke in the United States in 1952 amounted to 68,250,000 tons. The tar and light oil are prolific sources of benzene, naphthalene and other prime chemicals used in the synthesis of a broad range of aromatic organic chemicals.

The coke made in chemical-recovery coke ovens is in the form of dark gray blocks of irregular size and shape. Due to its cellular structure, coke is quite light, with apparent specific gravity usually in the range of 0.8 to 1.0. After quenching, coke is screened into various sizes depending on the intended use. Very small coke (under $\frac{1}{2}$ inch) is known as "breeze". The ash content of coke is approximately $\frac{1}{3}$ greater than that of the coal from which it is made, since all the coal ash remains in the coke. The volatile matter in high-temperature coke is usually under 1.5%.

The major use for coke in the United States is the reduction of iron ore to pig iron in blast furnaces. Much smaller amounts are utilized for the melting of iron or other metals in foundry cupolas, for the manufacture of water gas and producer gas, and for house heating. Since the steel industry uses 85% of the coke produced in the United States, production of coal chemicals is dependent to a very large degree on the rate of steel manufacture. The economics of chemical-recovery coke ovens rest very largely on the financial return from the coke.

ALFRED R. POWELL

Cross-references: *Fuels, Aromatic Compounds*

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COAL TAR *see* **DYES, ORGANIC CHEMISTRY, COAL AND COKE**

COBALT AND ITS COMPOUNDS

The metallic characteristics of cobalt are sharply defined, since it is in group VIII of the Periodic System, between iron and nickel. Though its compounds are similar to those of iron and nickel, unlike iron most of the important compounds are those containing bivalent cobalt (cobaltous). Though the trivalent cobalt compounds (cobaltic) are known, they have not been frequently used except in the form of coordination compounds where they have been studied very extensively.

The toxicity aspects of cobalt center around its ability to accelerate the formation of red blood cells and hemoglobin in the human system. Some catalytic action of the cobalt is suspected since it cannot be detected in the blood spectroscopically. The effect is a discharge of erythrocytes into the circulation because of the progressive hyperplasia (abnormal multiplication or increase in the number of normal cells) of the bone marrow. The increase in hemoglobin value is probably caused by the accelerated production of red blood cells by the bone marrow. The above mechanisms may occur to a serious degree upon exposure to substantial doses of soluble cobalt compounds or compounds which may be solubilized on introduction into the body.

The Fischer-Tropsch synthesis, in which carbon monoxide and hydrogen are combined to form organic compounds, is the major process using nonexpendable cobalt catalysts (cobalt driers, where the cobalt is expendable are discussed elsewhere). Thus, though cobalt catalysts have been examined in connection with many reactions, the work conducted by Fischer and Tropsch in Germany has been the only one which has expanded into a really substantial industrial operation. Both in the U. S. and Germany, the process has flourished and many catalysts, using various metals mixed with cobalt oxide, have been evaluated and used. Cobalt nitrate is frequently used as the starting compound and this is frequently precipitated along with thorium nitrate and finally admixed with such carriers as magnesium oxide and silica. The reduced form, of course, is the one that is used.

Colors containing cobalt have continued to be popular over the thousands of years. Cobalt aluminates and silicates are used, the oxide being the normal source, and cobalt concentration in the final color varies enormously, assaying as high as 60% and as low as 1%. As would be expected, the complexity of modern color requirements has resulted in the use of many other metal compounds along with the cobalt in order to produce the desired shades.

In the porcelain enamel industry, quite apart from the interest in the handsome colors secured with cobalt, is the need for excellent adhesion of the glass to the metal underbase. It has been found that a "grip-coat" usually applied underneath a white "cover-coat" and which usually comprises a glass of alumina, borax, silica, potash, soda ash, lime, and some fluorides, in which from 0.5 to 2% of cobalt is present as cobalt oxide, serves as an excellent underbase. The glass is manufactured at a relatively high temperature (1260-1315°C) but it may be finally fused to the metal to produce a coat of enamel at a temperature as low as 705-925°C and still produce excellent adhesion.

The ability of cobalt salts, especially the chloride, to change from the blue anhydrous form to red, when the humidity is sufficiently high, has made these compounds very useful as visual indicators of humidity. Test papers have been offered and silica gel and alumina have often been impregnated with small quantities of cobalt salts to indicate when the absorbent present is no longer effective as a dehydrator. With the increasing control over humidity, which modern industrial practice has more and more frequently demanded, these indicators, though representing a small total volume, are becoming increasingly important.

Because of the low order of reactivity of cobalt metal with organic acids, various inorganic cobalt compounds are used to prepare the salts of acids such as rosin acids, naphthenic acids and fatty acids. These soaps, being oil-soluble, enjoy a very large volume because of their potent effect on the "drying" process, the conversion of the liquid unsaturated oils, such as linseed or soybean, to a solid, useful film. Both "fused" soaps, in which the hydroxide is fused into suitable organic acids at temperatures in the range of 150°C, and "pre-

precipitated" soaps, in which a water solution of the sodium salt of the organic acid is reacted meta-thetically with a water-soluble cobalt salt, have been widely used as driers in paints. Cobalt concentrations from perhaps 1 to 14% are frequently encountered in this field.

Though animal nutritional deficiencies have received important attention only in recent years, the effect of trace amounts of certain elements is startling. Thus, cobalt deficiencies throughout the world have resulted in cattle and sheep showing long rough coats, scaliness of the skin, loss of flesh, pale mucous membranes, muscular incoordination, gauntness, retarded growth, and decreased milk flow. Curiously, though most of the cobalt administered is rapidly eliminated in the feces and in the urine, the animals' metabolic processes are enormously affected, possibly by modifying enzymic reactions through catalysis in the stomach and colon. At any rate, the animal's appetite and the amount of hemoglobin that is present in the blood rapidly reflects the appearance of cobalt in the diet.

The 1-5 mg. of cobalt per day necessary to keep sheep and cattle in good condition is far below the level which might produce an excess in the number of red corpuscles in the blood, and even levels as high as 50 mg. a day appear to exhibit no toxicity. Any of the common cobalt compounds which are water-soluble or which may become solubilized in the animal's stomach appear to be satisfactory, so it does not appear to matter whether the cobalt is administered in the feed, the drinking water or through salt blocks. Because of the acceleration of the rate of formation of red blood cells and hemoglobin, cobalt compounds have been used as therapeutic agents in the treatment of simple nutritional anemias. It is interesting to note that cobalt has proven to be a constituent of vitamin B₁₂, which is the antianemia principle of the liver. The table below presents the approximate poundage of the important cobalt salts manufactured in the U. S. in 1952-1953, as reported by the U. S. Bureau of Mines, together with typical prices.

Cobalt Compound	1953 Production, lb	1955 Price Per Lb
Acetate	104,913	\$1.30
Carbonate	111,408	1.935
Chloride	a	1.20
Hydroxide	255,386	2.72
Nitrate	a	1.00
Oxide	670,582	1.96
Phosphate	a	1.69
Sulfate	638,137	.89
Other compounds	250,092	—

S. B. ELLIOTT

Cross-references: *Driers, Metallic Soaps*

COEFFICIENTS

A coefficient may be defined broadly as a joint agent or that which unites in action with something else to produce an effect. Mathematically speaking, a coefficient is any numerical or literal

symbol or combination of symbols placed before another symbol or combination of symbols as a multiplier. As used in chemistry or physics a coefficient is a number expressing the amount of some change or effect under certain specified conditions as to temperature, pressure, length, concentration, volume, etc. The term is also used to designate the amount of change or effect so described.

Many coefficients are listed in technical and scientific literature. We will list a few: absorption, activity, alienation, compressibility, contraction, correlation, depression, diffusion, discharge, displacement, distribution, efficiency, efflux, elasticity, elastic resilience, expansion, firmness, fluidity, friction, homology, hygroscopicity, hysteresis, impact, intelligence, Joule-Thomson effect, kinematic viscosity, leakage, molecular, depression, partition, Peltier effect, purity, reduction, reflection, refraction, resilience, resistance, restitution, rigidity, safety, surface discharge, transmission, variability, variation, velocity, viscosity, volume elasticity, connection, and inertia. This article will select two of the coefficients and treat them so as to show the significance of a coefficient and the manner in which it is obtained.

Joule-Thomson Coefficient. The Joule-Thomson coefficient μ is found by measuring the temperature change from T' to T when the pressure P' of a gas on one side of a porous plug changes to P on the other side. The change of temperature ($T' - T$) and of ($P' - P$) are measured under conditions such that no heat is gained or lost by the gas, i.e., the process is adiabatic, and the pressure of the plug is great enough to insure a nearly constant pressure in the incoming and outgoing gas. The ratio of ($T' - T$)/($P' - P$) at several pressure ranges is extrapolated to the limiting case as ($P' - P$) approaches zero. This limiting value is the Joule-Thomson coefficient, μ . Thus

$$\mu = \frac{\partial T}{(\partial P)_H} \quad (1)$$

The subscript H indicates that the enthalpy, H , remains constant during the expansion ($\Delta H = 0$). The Joule-Thomson coefficient can be found for any fluid substance. In words, the coefficient is the change in temperature per atmosphere change of pressure on a gas or other fluid when the enthalpy remains constant.

For an ideal gas there is no attractive forces among molecules and hence no change of temperature with pressure and consequently $\mu = 0$. Hydrogen and helium at ordinary temperatures become warmer when forced through a porous plug and μ has negative values. However, below 154°K, μ becomes positive for hydrogen and the gas is cooled by free expansion. The values of μ for all gases become positive at sufficiently low temperatures. The value for air is +0.4 at 0°C.

The Joule-Thomson coefficient is used for calculations of industrial importance as in liquefaction of gases, and for calculations of many thermodynamic quantities and the constants in the equations of state for gases.

Activity Coefficient. In general, the activity coefficient of a substance may be defined as the ratio of the effective contribution of the substance to a phenomenon to the actual contribution of the substance to the phenomenon. In the case of gases the effective pressure of a gas is represented by the fugacity f and the actual pressure of the gas by P . The activity coefficient, γ , of the gas is given by $\gamma = f/P$.

One method of calculating fugacity and hence γ is based on the measured deviation of the volume of a real gas from that of an ideal gas. Consider the case of a pure gas. The free energy F and chemical potential μ changes with pressure according to the equation

$$dF = d\mu = V dP. \quad (2)$$

but by definition

$$d\mu = V dP = RT d \ln f \quad (3)$$

If the gas is ideal, the molal volume V_i is given by

$$V_i = \frac{RT}{P} \quad (4)$$

but for a nonideal gas this is not true. Let the molal volume of the nonideal gas be V_n and define the quantity α by the equation

$$\alpha = V_n - V_i = \frac{RT}{P} - V_n \quad (5)$$

Then V of equation (2) is V_n of equation (5) and hence from equation (5)

$$V = \frac{RT}{P} - \alpha \quad (6)$$

Therefore from equations (2), (3), and (6)

$$RT d \ln f = dF = d\mu = RT d \ln P - \alpha dP \quad (7)$$

and

$$RT \ln f = RT \ln P - \int_0^P \alpha dP \quad (8)$$

Thus knowing PVT data for a gas it is possible to calculate f . The integral in equation (8) can be evaluated graphically by plotting α , the deviation of gas volume from ideality, versus P and finding the area under the curve out to the desired pressure. Also it may be found by mathematically relating α to P by an equation of state, or by using the method of least squares or other acceptable procedure the integral may be evaluated analytically for any value of P . The value of f at the desired value of P may thus be found and consequently the activity coefficient calculated. Other methods are available for the calculation of f and hence of γ , the simplest perhaps being the relationship

$$f = \frac{P_i}{P} \quad (9)$$

where P_i is the ideal and P the actual pressure of the gas.

In the case of nonideal solutions, we can relate the activity a_A of any component A of the solution

to the chemical potential μ_A of that component by the equation

$$\mu_A = \mu_A^0 + RT \ln a_A \quad (10)$$

$$= \mu_A^0 + RT \ln \gamma_A X_A \quad (11)$$

where μ_A^0 is the chemical potential of component A when its mole fraction X_A in the solution is unity, i.e., when the liquid is pure component A . γ_A is the activity coefficient of component A in the solution and is given by the expression

$$\gamma_A = \frac{a_A}{X_A} \quad (12)$$

In equation (12) a_A is the activity or in a sense the effective mole fraction of component A in the solution.

The activity a_A of a component A in solution may be found by considering component A as the solvent. Then its activity at any mole fraction is the ratio of the partial pressure of the vapor of A in the solution to the vapor pressure of pure A . If B is the solute its standard reference state is taken as a hypothetical B with properties which it possesses at infinite dilution.

The equilibrium constant for the process



is

$$K = \frac{a_{\text{solution}}}{a_{\text{gas}}} \quad (14)$$

Since the gas is sufficiently ideal its activity a_{gas} is equivalent to its pressure P_2 . Since the solution is far from ideal, the activity a_{solution} of the liquid B is not equal to its mole fraction N_2 in the solution. However,

$$K' = N_2/P_2 \quad (15)$$

and extrapolating a plot of this value versus N_2 to $N_2 = 0$ one obtains the ratio where the solution is ideal. This extrapolated value of K' is the true equilibrium constant K when the activity is equal to the mole fraction

$$K = a_2/P_2 \quad (16)$$

Thus a_2 can be found. The methods involved in equations (13) through (16) arrive at the activities directly and thus obviate the determination of the activity coefficient. However, from the determined activities and known mole fractions γ can be found as indicated in equation (12).

In the case of ions the activities, a_+ and a_- of the positive and negative ions, respectively, are related to the activity, a , of the solute as a whole by the equation

$$a_+^p \times a_-^q = a \quad (17)$$

and the activity coefficients γ_+ and γ_- of the two charge types of ions are related to the molality, m , of the electrolyte and ion activities a_+ and a_- by the equations

$$\gamma_+ = \frac{a_+}{pm}; \quad \gamma_- = \frac{a_-}{qm} \quad (18)$$

Also the activity coefficient of the electrolyte is

given by the equation

$$\gamma = (\gamma_+^p \times \gamma_-^q)^{1/(p+q)} \quad (19)$$

in equations (17), (18) and (19) p and q are numbers of positive and negative ions, respectively in the molecule of electrolyte. In dilute solutions it is considered that ionic activities are equal for uni-univalent electrolytes, i.e., $\gamma_+ = \gamma_-$.

Consider the case of BaCl_2 .

$$\gamma = (\gamma_+ \times \gamma_-^2)^{1/(1+2)} = (\gamma_+ \times \gamma_-^2)^{1/3} \quad (20)$$

or

$$\gamma^3 = \gamma_+ \gamma_-^2 \quad (21)$$

also

$$a = a_+ \times a_-^2 = (m\gamma_+) (2m\gamma_-)^2 \quad (22)$$

$$= 4m^3\gamma_+\gamma_-^2 = 4m^3\gamma^3 \quad (23)$$

Activity coefficients of ions are determined using electromotive force, freezing point, and solubility measurements, or are calculated using the theoretical equation of Debye and Hückel.

The solubility, s , of AgCl can be determined at a given temperature and the activity coefficient γ determined at that temperature from the solubility and the solubility product constant K . Thus

$$K = a_+a_- = \gamma_+c_+\gamma_-c_- \quad (24)$$

where c_+ and c_- are the molar concentrations of the positive silver and negative chloride ions, respectively. The solubility s of the silver chloride is simply $s = c_+ = c_-$. The expression for K is then

$$K = \gamma^2s^2 \quad (25)$$

and

$$\gamma = \frac{K^{1/2}}{s} \quad (26)$$

By measuring the solubility, s , of the silver chloride in different concentration of added salt and extrapolating the solubilities to zero salt concentration, or better, to zero ionic strength, one obtains the solubility when $\gamma = 1$, and from equation (26) K can be found. Then γ can be calculated using this value of K and any measured solubility. Actually, this method is only applicable to sparingly soluble salts. Activity coefficients of ions and of electrolytes can be calculated from the Debye-Hückel equations. For a uni-univalent electrolyte, in water at 25°C, the equation for the activity coefficient of an electrolyte is

$$\log \gamma = -0.509z_+z_- \sqrt{\mu} \quad (27)$$

where z_+ and z_- are the valences of the ion and μ is the ionic strength of the solution, i.e.,

$$\mu = \frac{1}{2} \sum c_i z_i^2 \quad (28)$$

where c_i is the concentration and z_i the valence of the i th type of ion.

Activity coefficients are used in calculation of equilibrium constants, rates of reactions, electrochemical phenomena, and almost all quantities involving solutes or solvents in solution.

EDWARD S. AMIS

Cross-references: *Solutions, Debye-Hückel Theory, Electrochemistry, Activity*

COLCHICINE

Colchicine is an alkaloid drug, obtained from crocus plants (especially *Colchicum autumnale*), which is notable chiefly for its remarkable utility in plant breeding. In 1937, it was discovered that a dilute solution of colchicine introduced into the growing parts of plants was capable of interfering in the normal sequence of events which take place during cell division. The result was an exact doubling of the amount of hereditary material in the cell nucleus. During division, the hereditary material is visible as a number of elongated microscopic structures called chromosomes. On the chromosomes, in bead-like arrangement, are the specific units which control the detail of inheritance—the genes.

Colchicine's effect is registered at the stage in division when the split-apart chromosome halves, which ordinarily move away from each other to form two new nuclei, fail to become separated and therefore remain in the original nucleus as it returns to a nondividing condition. After the colchicine has disappeared from the cell the process of division is initiated again, this time, however, with twice the normal number of chromosomes. This and succeeding divisions proceed without interruption, and the result is the perpetuation of the new double number of chromosomes.

From colchicine treatments of seeds or of growing regions in stem or root, large areas of new tissue may be built up from cells whose nuclei have the doubled, or "tetraploid" as distinguished from the normal, or "diploid" number of chromosomes; or, as sometimes happens, complete or nearly complete conversion to the tetraploid condition results throughout the plant. Then, if flowers arise from tetraploid tissue, it is possible to perpetuate the increased number of chromosomes through the seed.

Plants with the tetraploid number of chromosomes almost always have larger cells. An advantage much capitalized upon in breeding is a frequent enlargement effect upon those plant organs, such as flowers, fruits and seeds, which complete their growth in a single season. Colchicine treatment has been tried with a great variety of plant species, including fruits and vegetables, flowers, forage, range and pasture plants, forest trees, sugar beets, cotton and tobacco. Tetraploid snapdragons are an example of plants now in commercial production which owe their origin to colchicine treatment of diploid forms. Colchicine has also been used to make certain sterile hybrids fertile, which carries the possibility of making a new species. Since colchicine's effect is upon the hereditary material, it is not, as often popularly supposed, a vitamin or a chemical fertilizer or weed killer.

Chemically, colchicine is $\text{C}_{22}\text{H}_{26}\text{O}_6\text{N}$. Its structure is still under investigation, but is known to involve three rings. Its value is due in part to an unusually high solubility in water, and it is soluble, as well, in alcohol, chloroform and lipoids, such as lanolin. Colchicine is also a tool for the study of plant evolution, and for various kinds of experimental study of growth in animals, includ-

ing cancer investigations. No completely polyploid animals have yet been produced, using colchicine, but partially polyploid rabbits, pigs and frogs have resulted. Though long used to treat gout, it is a potent human poison in slightly higher concentrations, and has specific effects upon nervous systems, liver, blood and muscle.

PHILIP N. JORANSON

Cross-references: *Alkaloids*

COLLOID CHEMISTRY

The word "colloid", even in the relatively brief period since Thomas Graham proposed it, has acquired a meaning far wider and more significant than he had remotely imagined. It now covers innumerable materials as different from glue, the equivalent of the Greek word from which colloid is derived, as are Purple of Cassius and such everyday colloids as soap solutions, rayon and bakelite. In fact, colloids constitute most of the materials of ordinary life. The broadest definition of colloid science is the study of noncrystalline matter having an organization intermediate between that of independent molecules and of living matter. It is inadequate to define colloids as being composed of particles with at least one dimension lying between 10 angstroms and 1 micron. Actually colloidal matter consists of three coordinating factors: (1) particles, (2) a continuous medium, and (3) a stabilizing agent.

About 100 years ago, several leading chemists, while studying precipitation reactions of compounds insoluble in water, such as arsenic trisulfide and Prussian blue, observed that apparently no precipitate formed when they used a low concentration of reactants. The liquid took on the color that was characteristic of the normal precipitate but otherwise remained perfectly clear and transparent to the eye of the observer. Berzelius, the only one who tried to explain the paradox, assumed the particles of the formed precipitate to be very small and transparent. Solutions of this type were termed "pseudosolutions". It then became evident that the clear but vividly colored solutions of precious metals (*aurum* and *argentum potabile*), which the alchemists had prepared and for which they claimed exceptional healing power, must be classified in the same group, for these solutions had been obtained by reducing a dissolved gold or silver salt to the elementary and therefore water-insoluble metal.

In 1857 Michael Faraday demonstrated visually a striking difference between a true solution and a pseudosolution. If a concentrated beam of light is passed through the former (in a darkened room), its path through the liquid cannot be detected; but if a "pseudosolution" is substituted, the passage of the light beam is clearly observed. Millions of particles, suspended in the liquid (or in air) reflect the light impinging on them, but are too small for the human eye to perceive (Tyndall effect).

In 1861 Thomas Graham, studying the rate of diffusion of a solution of a water-soluble substance into a volume of pure water, noticed that

matter which has the aptitude for crystallizing diffuses rapidly, whereas more gelatinous substances such as glue diffuse either very slowly or not at all. Having found other substances which behaved "like glue" he coined for them the term "colloid". In contrast, he named rapidly diffusing substances "crystalloids". The difference in rate of diffusion was first attributed to a difference in size between colloidal particles and those constituting a true solution. This reasoning and the development of the ultramicroscope by Zsigmondy (1903), which made possible the actual detection of discrete individual particles in a colloidal solution, resulted in a belief that still frequently prevails: that colloids are nothing but extremely small particles suspended in a fluid.

This belief takes into consideration only part of the picture, however. If we roll and hammer a piece of gold until it becomes so thin that we can no longer measure its thickness with an ordinary microscope it still looks like a golden sheet. Such treatment does change one property of the original specimen, however: the formed film has become transparent. There is no distortion of the shape of objects seen through it, but they are all bathed in a beautiful green color. Most catalysts increase in activity with decreasing particle size, reaching a maximum in the colloidal range. Many other properties could be listed which exhibit pronounced maxima or minima as soon as the substance, like the transparent gold, has been brought to very minute dimensions. Can we offer an explanation for such sudden changes in property?

The smallest dimensions which can be resolved with a regular microscope are 0.001 mm, or 1 μ . Simple chemical molecules which diffuse rapidly will be at least a thousand times smaller, 0.000001 mm, or 1 $\mu\mu$. This dimensional range, in which matter exhibits specific properties, is termed the "colloidal range of dimensions". Colloid chemistry is the study of properties of matter present in the colloidal range in at least one of its three possible dimensions. Colloid chemistry may therefore not be regarded as the chemistry of a specific type of substance, such as matter of organic or inorganic composition. It is the chemistry of a state of matter characterized by a preponderance of surface over volume. Taking into account the fact that a difference in chemical saturation must exist between an ion located in the interior of a structure, let us say in a crystal, and an ion located at its surface, we immediately realize the importance of such surface developments. Since unsaturation may be regarded as synonymous with reactivity, the increase of reactivity with decreasing dimensions becomes a logical consequence.

In the range of colloidal dimensions the surface development and the importance of all energy located therein have become predominant. If comminution were to be continued, the dimensions of simple molecules, atoms, etc., would be reached, where the expression "surface", as generally used, becomes meaningless. We are therefore justified in calling colloid chemistry also the *chemistry of surfaces and surface reactions*. The regular chemist is primarily interested in the composition of the bulk phase of matter, the

mineralogist in the crystal configurations of matter, the physicist in the physical properties of matter present in bulk form; but the colloid chemist is primarily concerned with the composition and reactivity of the surface layers of matter and the changes which they undergo.

A great many substances of colloidal dimensions, on being suspended in water, owe their stability to electric charges located at their surfaces which repel all other particles of the same sign of charge. If these charges are neutralized by charges of opposite sign, the stability of the suspension is destroyed and the system precipitates. Systems of this kind are termed *electrocratic* colloids (for example, the "drinkable gold" of the alchemists). Other colloids, generally of organic origin, owe their stability to their great affinity to the liquid in which they are dispersed and are not affected by the addition of substances which neutralize surface charges. These are known as *lyocratic* colloids. If we coat an electrocratic colloid with a lyocratic one we change the surface of the former and produce, to all intents and purposes, a colloidal dispersion of lyocratic properties. This dispersion will not be affected by electrolytes—we have "protected" the electrocratic colloid.

If we mix oil and water and agitate the mixture violently we form what is known as an emulsion. As soon as the agitation ceases the two liquids will separate again. If we add a soap, however, the emulsion becomes stable. Stability occurs because the soap molecules line up (adsorb) on the surface of the oil droplets in an oriented fashion, one portion of each soap molecule lying in the water, the other portion being embedded in the oil; a new surface possessing repulsive energy has been formed.

A better understanding of surface and interfacial tension, and of wettability, which depends on it, is also necessary. Again the arrangement of molecules in the surface layer of colloidal thickness controls the phenomenon. If on the surface of a material which is not readily wetted by, let us say, water, a substance is adsorbed which because of its molecular configuration has an affinity for both the material and for water, the result is a wettability that is notably augmented.

The study of the mechanism which causes colloidal dispersions to gel is constantly increasing in importance, for only the final solution of this question will provide the answer to the most fundamental biologic questions of cell life, cell division and life in general. Since the human body is composed largely of matter in the colloidal state, it is only logical that a well-founded knowledge of colloidal phenomena is essential whenever problems of avoiding or repairing damage are involved; to quote Leonard Thompson Trolant: "It is to colloidal chemistry that we must look for answers to the large majority of the fundamental problems of vital activity. These answers will be slow in appearing, however, if we refuse to look".

It must not be forgotten that protoplasm, a colloid, is the material basis of life. Since it is very probable that protoplasm has thixotropic properties, this phenomenon may not be neglected in any biologic investigation. "Thixotropy" is the

term used to describe an isothermal, reversible, sol-gel transformation: the gel may be liquefied to a sol simply by agitation, and the sol sets to a gel again when left at rest. There is now ample evidence that the interior of muscle fibers and the protoplasm of myxomycetes, to mention only two, have pronounced thixotropic properties.

That colloid chemistry should find more appreciation in medical science than it has thus far received is perhaps best illustrated by giving just one example.

An application of colloid chemistry to medicine is found in recent investigations that have introduced this branch of science into the field of antibiotics. Thus far considerable emphasis has been placed on a strictly chemical approach to the study of antibiotics in general and of penicillin in particular. However, examination from a colloidal approach reveals that various antibiotics possess properties which are very peculiar from a physicochemical, but not from a colloid-chemical point of view. For example, until recently it was generally assumed that penicillin, when dissolved in water, formed a true solution. That this is true has been disproved by ultramicroscopic studies which show that such solutions are actually colloidal (sols). It has also been shown that aqueous solutions of sodium penicillin possess high capillary activity, which means that they greatly reduce the surface tension of water. Penicillin solutions possess greater wetting properties than solutions of other antibacterial substances, manifesting less surface activity, and therefore can be expected to diffuse throughout tissue more readily than the latter.

In its colloidal behavior penicillin resembles soaps and may be regarded as a colloidal electrolyte. Considering the morphology of the colloidal micelle of a penicillin salt and comparing it with that of a soap micelle oriented in an oil-water interface, the antibiotic action might to some degree resolve itself into a surface phenomenon comparable to the formation of a stable emulsion. The emulsified droplet, having lost all the properties and chemical reactivity of the substance which has been emulsified, assumes the qualities and properties of the emulsifying agent. Thus, it is conceivable that adsorption of the penicillin micelle onto the surface of the bacterial cell could play a part in the mode of action of that antibiotic. It is also conceivable, although at present a conjecture, that electrokinetic phenomena may somehow enter into the relationship of penicillin to the bacterial cell, since electrophoresis experiments have shown that the penicillin micelle possesses a net negative charge.

Another proof that colloid science deserves far more attention than it has so far received is the development of a clay of the bentonite type which will exhibit thixotropic properties only when dispersed in an organic solution, like toluene. The original clay, a sodium-bentonite, has been reacted with an organic compound, an amine, so that its surface now carries the adsorbed amine molecules which cause the reactivity with the organic solvent. The interior of the colloidal particle remains strictly a clay particle, however,

composed of silica and alumina; only the surface of the particle has been reacted with the organic amine.

ERNST A. HAUSER

Cross-references: *Clays, Antibiotics, Emulsions, Surfactants, Adsorption, Gels*

COMBINING NUMBER

The combining number of an element or a radical is a small whole number used in writing formulas. It is sometimes called the valence (number). Hydrogen is usually taken as the standard of combining numbers with value equal to 1.

(1) The number of hydrogen atoms that an element combines with directly is called its combining number. The compounds hydrogen chloride (HCl) and sodium hydride (NaH) are relevant examples. The formulas are derived from experimental data. In hydrogen chloride, one atom of hydrogen combines with one atom of chlorine. The combining number of chlorine is 1. Using similar reasoning, sodium also has combining number 1 because it combines with one atom of hydrogen. The compound between sodium and chlorine is written NaCl, each element having combining number 1. This formula (NaCl) for sodium chloride is verified by analysis. It contains 39.3% of sodium and 60.7% of chlorine— the proper amounts if this compound has a 1 to 1 relationship between the number of atoms. From the formulas of the compounds water (H₂O), ammonia (NH₃), and methane (CH₄) it is clear that the combining number of oxygen is 2, nitrogen 3, and carbon 4.

Hydrogen is believed to have one electron in its K shell. It may fill the shell by borrowing or by sharing electrons as it does in NaH (borrowing); or it may lose its electron as it does in hydrogen chloride, where the electron pair that constitutes the bond probably is closer to the chlorine than to the hydrogen nucleus, electrically considered. In the first case the combining number of hydrogen is 1- and in the second case it is 1+. In general, negative combining numbers refer to elements that have gained electrons, and positive numbers to elements that have lost electrons. If a covalent electron pair is nearer one nucleus than another, the nearer nucleus is considered to be negatively charged.

(2) Certain unit groups of elements stay together during many chemical changes. These groups are called *radicals*. The number of hydrogen atoms with which a radical combines directly is its combining number. From the formulas HNO₃, nitric acid; H₂SO₄, sulfuric acid; H₃PO₄, phosphoric acid, it can be seen that the combining number of the nitrate radical (NO₃) is 1, that of sulfate radical (SO₄) is 2 and that of phosphate radical (PO₄) is 3.

(3) Combining numbers may be inferred by substitution. Not all elements readily combine directly with hydrogen. Silver is such an element. The formula of silver nitrate is AgNO₃. When this formula is compared with that of nitric acid (HNO₃), it is evident that one atom of silver replaces one atom of hydrogen. Since silver has re-

placing value equivalent to hydrogen atom for atom, the combining number of silver is therefore 1. Similarly, when CuSO₄ and H₂SO₄ are compared, it can be seen that a copper atom has taken the place of two hydrogen atoms, and therefore copper has combining number 2. In a similar manner, the combining number of every element or radical may be determined.

According to theory, the combining number of elements in ionic compounds is the number of electrons transferred. It has the same value as the charge on the ion of that element. Calcium chloride (CaCl₂) is such an ionic compound in which the two chlorine atoms have gained one electron each from the calcium atom, which is thereby charged two units positive, or Ca⁺⁺. Both of the chlorine atoms gain one electron each, becoming chloride ions (Cl⁻). The combining number of calcium is 2, and that of chlorine is 1.

For covalent compounds, the combining number is the same as the number of shared electron pairs. In carbon disulfide (CS₂), carbon shares its four electrons with the two sulfur atoms, two pairs to each. The combining number of carbon is 4 (four shared electron pairs), and the combining number of sulfur is 2 (two shared electron pairs).

It is well known that many elements exhibit more than one combining number, nitrogen, chlorine, manganese, molybdenum and chromium being among those that are especially noted for this property. The combining number depends on how many electrons in the outermost shell of an element are involved, or how many electrons it can draw up from or depress to lower levels.

ELBERT C. WEAVER

Cross-references: *Bonds, Valence, Combining Weight, Formulas*

COMBINING WEIGHT

The combining weight (or equivalent weight) of an element is found as one step toward determining its atomic weight by a chemical method. Most of the atomic weights today are found by use of the mass spectrograph, which also gives information about the isotopes present and their relative abundance. The chemical methods of finding atomic weights are fast becoming of only historical interest.

Although any weight of any element may be selected as a standard for combining weights, experience shows that exactly 8 grams of oxygen is the most satisfactory standard. Oxygen combines directly with many metals and nonmetals. The combining weight of an element may be defined as the weight of that element that combines with 8 g of oxygen, or its equivalent. Since 8 g of oxygen combines with 1.008 g of hydrogen, the latter is considered equivalent to 8 g of oxygen. When the value of 8 g is selected for the combining weight of oxygen, no element has a combining weight value less than 1.

The task of finding combining weights consists of measuring with some precision the weight of the element that combines with 8 grams of oxygen. For elements that do not combine readily with

oxygen, the weight of that element that combines with 1.008 g of hydrogen, or replaces that weight of hydrogen from an acid, may be found. In many cases, different weights of an element may combine with 8 g of oxygen. In such cases, the element has more than one combining number.

The facts needed to find a combining weight may be measured in the laboratory. For example: 8 g of oxygen combines completely with 12.16 g of magnesium when the two elements combine. Hence the value 12.16 is accepted as the combining weight of magnesium.

In another experiment more frequently performed, the combining weight of magnesium is found by measuring the volume of hydrogen that magnesium replaces from acid, finding the weight of the hydrogen, and calculating the weight of magnesium needed to produce 1.008 g of hydrogen. In this case, a piece of magnesium is used that weighs 0.0960 g. The metal is immersed in dilute acid and all the hydrogen released is collected in a gas-measuring burette. The volume of gas at standard temperature and pressure, after the necessary corrections have been applied, is 88.4 ml, or 0.0884 liter. Hydrogen weighs 0.0899 g/liter (its density at STP), so the weight of hydrogen is 0.0884 liter \times 0.0899 g/liter, or 0.00795 g.

If 0.0960 g of magnesium released 0.00795 g of hydrogen, then the weight of magnesium that can release 1.008 g of hydrogen is found by the proportion

$$\frac{0.096 \text{ g}}{x} = \frac{0.00795 \text{ g}}{1.008 \text{ g}}$$

The value for x , the combining weight of magnesium, is 12.17 from the solution of this proportion. The accepted value is 12.16.

The combining weight is now used to find the atomic weight of magnesium as follows: According to the law of Dulong and Petit, the atomic weight \times specific heat = 6.4. The results from the use of this law are necessarily approximate because the specific heat varies with the temperature, state of matter, and other factors. For metals, however, application of the law gives an approximation that shows the order of magnitude of the correct value of the atomic weight.

The specific heat of magnesium is 0.25 (cal/g/ $^{\circ}$ C). Atomic weight of magnesium = $6.4/0.25$, or 25.6, that is, the atomic weight of magnesium is approximately 25.6. Since $25.6/12.17$ is approximately 2, the combining weight of magnesium should be multiplied by 2 to find the atomic weight. In this case $12.17 \times 2 = 24.34$, atomic weight of magnesium. The accepted value in the International Table, based on more exact work, is 24.32.

Other experiments show that 1.008 g of hydrogen is equivalent to 35.457 g of chlorine when the two elements combine directly. Likewise 1.008 g of hydrogen is equivalent to 79.916 g of bromine.

According to the experiments of Richards and Cushman, an average of 8 trials, 24.28947 g of highly purified nickel bromide produced 6.52235 g of metallic nickel when the bromide was reduced with hydrogen. The weight of bromine present is found to be 17.76612 g (by subtracting, $24.28947 - 6.52235$). The ratio of bromine to nickel is 17.76612/

6.52235. If we accept 79.916 as the combining weight of bromine, then the combining weight of nickel is found by the proportion $17.76612/6.52235 = 79.916/x$; $x = 29.341$, the combining weight of nickel.

The specific heat of nickel is about 0.11. Applying the law of Dulong and Petit we get atomic weight $\times 0.11 = 6.4$. The atomic weight of nickel is about 58.2. Since $58.2/29.341$ is approximately 2, $2 \times 29.341 = 58.682$, atomic weight of nickel. The accepted value in the International Table is 58.69.

ELBERT C. WEAVER

Cross-references: *Combining Number, Formulas*

COMBUSTION

Combustion in its broad sense includes not only the process of chemical combination with oxygen but also combination with chlorine and various other substances. Fire may be defined as rapid oxidation with the evolution of light and heat. Air contains approximately one-fifth oxygen and four-fifths nitrogen by volume. Except in a few special cases the nitrogen in the air does not enter the chemical reaction of combustion, and serves only to dilute the oxygen, thus reducing the intensity of combustion as compared with an atmosphere of pure oxygen. In an atmosphere of pure oxygen fires burn with greatly increased intensity, and some substances may ignite spontaneously at room temperatures.

Fire can continue only where there are present fuel, oxygen (or other oxidizing agent) from the air or other source, and a sufficiently high temperature to maintain combustion. Extinguishment can be accomplished by the elimination of any one of the three factors: by removing the fuel, by excluding oxygen (smothering), or by reducing the temperature (cooling by water or other means).

In the burning of most substances the actual combustion takes place only after the solid or liquid fuel has been vaporized or decomposed by heat to produce a gas, and the visible flame is the burning gas. However, in the case of solid fuels which do not evaporate or decompose to form gases at ordinary fire temperatures, combustion also takes place by direct combination of the fuel with oxygen, particularly in the case of the glowing combustion of charcoal or of charred wood remaining after combustible gases have burned.

Most ordinary combustible materials consist of compounds mainly composed of carbon and hydrogen. When materials burn in a free air supply the principal products of combustion are carbon dioxide and steam. With a restricted air supply carbon monoxide may be produced, but when subsequently in contact with additional oxygen the carbon monoxide will burn to form carbon dioxide (assuming a source of ignition).

A few materials such as pyroxylin plastic contain enough oxygen chemically combined so that partial combustion or decomposition may occur without oxygen from the air. Such materials cannot be extinguished by removal of oxygen supply (smothering), but only by cooling.

C. I. BABCOCK

Cross-references: *Autoignition Point, Fuels*

CONCRETE, see CEMENT, PORTLAND

CONDUCTANCE

When a strong electrolyte is dissolved in water, the solute consists of electrically charged molecules, called ions. If the solution is sufficiently concentrated, some of the oppositely charged ions associate giving, in effect, a neutral molecule of the dissolved electrolyte. Weak electrolytes behave as though a major part of the solute is in the molecular state while only a small fraction is ionized. When an electrical potential difference exists between electrodes in the solution, the positively charged ions (cations) flow toward the negative electrode, the cathode. The anions flow toward the anode. Thus a flow of electricity occurs in the solution and Ohm's law, $R = E/I$, applies. E is the difference in potential, I is the current strength and R is the resistance of the solution. The resistance of 1 cc of a solution between electrodes 1 cm apart is the specific resistance, \bar{R} , of the solution. The magnitude of the specific resistance is a function of several variables; the nature of the electrolyte, the concentration of the solution, temperature, etc. The magnitudes of some specific resistances are.

Silver	1.6×10^{-6}
NaCl (fused)	2.9×10^{-1}
1M KCl	8.9
0.001M KCl	6.8×10^3
0.001M CH_3COOH	2.4×10^4
Water	2.5×10^7

Resistance of solution measurements are usually made by means of a Wheatstone bridge, one arm of which is a conductivity cell containing the solution. Several characteristics of the bridge should be taken into consideration, depending upon the accuracy which is desired. A pure sine wave, low voltage and moderate frequency alternating current is generally employed. Six volts and 1000 cycles are satisfactory. At high voltages (20,000 volts) the Wien effect and at high frequencies (30,000 kilocycles) the Falkenhausen effect are encountered, giving extraordinary results. Alternating current is used to minimize polarization effects at the electrodes. Polarization effects are further minimized by using platinum electrodes coated with platinum black. Such electrodes have large surfaces and low overvoltage. The conductivity cell is designed so as to minimize capacity effects due to the filling tubes and the lead-in wires. Residual capacity effects are balanced out by including a variable capacitor across the decade resistance box which serves as one arm of the Wheatstone bridge. The resistance spools in this box should have a bifilar winding.

Special shapes are used in making the cell depending on the resistance of the solution to be measured. The dimensions of the particular cell are determined by filling it with a solution of known specific resistance (usually a KCl solution) and measuring the resistance. This gives a cell constant in terms of the dimensions of the cell. The null point in the Wheatstone bridge setting is determined by a telephone receiver tuned to the frequency of the current used. For less precise

measurements, the "electric eye" cathode tube may be used. Electric leakage is guarded against by carefully shielding the equipment. The conductivity cell is kept at constant temperature because the temperature coefficient of electrical resistance is quite high. When proper precautions are taken, the measurements of the resistance of solutions are classified as among the more precise physical chemical measurements.

The *conductance*, L , of a solution is defined as the reciprocal of the resistance, (1) $L = 1/R$. The specific conductance of a solution, (2) $\bar{L} = 1/\bar{R}$, is the conductance of 1 cc of the solution between electrodes 1 cm apart. It is a function of the same variables as is the resistance. The equivalent conductance, Λ , is of more theoretical significance than the specific conductance. The equivalent conductance is related to the specific conductance by the equations, (3) $\Lambda = V\bar{L} = 1000\bar{L}/c$, where V is the volume of the solution containing one equivalent weight of electrolyte and c is the normality of the solution. It is defined as the conductance of a solution which contains one equivalent weight of electrolyte between electrodes one cm. apart.

Kohlrausch, who pioneered in the field of electrical conductance measurements, established the relationships, (4) $\bar{L} = l_+ + l_-$ and (5) $\Lambda = \lambda_+ + \lambda_-$; that is, the conductance of a solution of an electrolyte is the sum of the conductance of the ions in that solution. The l 's are specific ion conductances and the λ 's are equivalent ion conductances. Ionic conductances are functions of transference numbers and of ionic mobilities. They may be evaluated from equivalent conductance and transference number data by means of the relationship (6) $l_+ = t_+ \Lambda$. Tables of ionic conductances are found in handbook literature.

For theoretical considerations the equivalent conductance at infinite dilution, Λ_0 , is an important function. This is defined as the equivalent conductance of a solution which is dilute enough so that further addition of solvent does not affect the conductivity. Its value cannot be measured directly because the concentrations of these very dilute solutions are so low that the physical measurements have a high degree of uncertainty. Its value is obtained by extrapolating values of Λ versus \sqrt{c} to zero concentration. These values of Λ 's are obtained by measurements on solutions which are sufficiently concentrated so that accurate data can be obtained. The Debye-Hückel theory, which applies to the dilute region in which the conductivity measurements are uncertain, shows that a straight-line extrapolation is valid. Conversely, conductance measurements on fairly insoluble salts have been fruitful in confirming the validity of the Debye-Hückel theory (which see).

The extrapolation method does not apply to solutions of weak electrolytes. In this case, not only does the uncertainty in the measurements occur at higher concentrations, owing to the low values of Λ , but also the values of Λ are changing with dilution so rapidly that the destination of the curve at zero concentration cannot be estimated. A second method is available for these cases as well as for the case of the strong electrolyte. This is the application of Kohlrausch's law, (7) $\Lambda_0 = \lambda_{0+} + \lambda_{0-}$. The values of the ion conductances at

infinite dilution have been determined by measurements of Λ 's for strong electrolytes and the value of the transference number of some strong electrolyte by means of the equation (8) $\lambda_{\text{O}^+} = \Lambda_{\text{O}^+} / t_{\text{O}^+}$.

The Onsager equation—a modification of the Debye-Hückel equation—is (9)

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{c},$$

where A and B are constants dependent on the solvent and on the temperature. A is a function of the dielectric constant and of the viscosity of the solvent and B is a function of the dielectric constant of the solvent. This equation is applicable to dilute solutions only. Some factors which cause deviations from the equation in more concentrated solutions are incomplete dissociation, yielding simple ions, intermediate ions, ion-pairs and neutral molecules, and the solvation of these charged and neutral molecules, thus changing the nature of both the solute and the solvent. These factors have not yet been satisfactorily evaluated.

In addition to the very extensive studies made on the conductance of aqueous solutions of electrolytes, much work has been done on the conductance of solutions in nonaqueous solvents and in mixed solvents. In these studies the unique effects can probably be attributed to variations in the dielectric constants and the viscosities of the solvents and to different degrees of solvation of the solutes.

Conductivity of solutions has been of practical value in several fields. One of the most important methods for determining the solubility of slightly soluble electrolytes is by measuring the conductance of their saturated solutions. In this case it is assumed that $\Lambda = \Lambda_0$ and equation (2) is applied to calculate the concentration. Conductance measurements are made to determine the end points in titrations. This is possible because of the difference in the mobilities of the ions formed or added as the titration proceeds. Conductance measurements are used in controlling the concentration of solution in chemical processes. In electrochemical processes the voltage drop across the electrolytic cell is composed of reversible and irreversible potential drops at the electrodes and of the potential drop required to overcome the ohmic resistance of the bath. Substitution of one electrolyte for another may substantially change the magnitude of this last component.

W. W. EWING

Cross-references: *Debye-Hückel Theory, Electrolysis, Ionization, Ions, Solutions, Electrochemistry*

CONDUCTOMETRIC TITRATIONS

Conductometric titrations are titrations in which the end-point determination depends upon a change in conductivity of the solution being titrated. The method depends upon the involvement of ions in the titration reaction such that rate of change of the conductivity changes at the end point. The individual ion equivalent conduc-

tivities at infinite dilution for a series of ions are:

H ⁺	315.2	OH ⁻	173.8
Li ⁺	33.0	Cl ⁻	65.5
Na ⁺	43.2	Br ⁻	67.3
K ⁺	64.2	I ⁻	66.3
Ca ⁺⁺	51.9	SO ₄ ⁻	68.5
Ba ⁺⁺	55.4	NO ₃ ⁻	61.6

The conductivities of the salt or acid solutions formed from these ions are roughly proportional to the sum of the individual ion conductivities.

For example, if an acid is titrated with a base, the conductivity of the acid is first measured; then as the base is added acid and base are converted to salt and undissociated water having a lower conductivity. Thus the conductivity is decreased as the acid is neutralized until the end point is reached. With the addition of more base, the conductivity rises again, due to the presence of the good conductor, hydroxyl ion, in the base. The original decrease in conductivity as the base is added is approximately linear, as is the subsequent (to the end point) increase in conductivity. Thus, if a plot is made of conductivity vs ml. base added, the lines before and after the end point may be extrapolated until they cross. The crossing point is the end point (Fig. 1).

A large number of reactions involving ions which are rapid and complete enough to be used quantitatively can be done conductometrically. Generally, rather concentrated solutions are used to get a good rate of change of conductivity as the titrant is added. The method is most accurate in titrations giving the largest change in rate of change of conductivity at the end point. Generally speaking, the accuracy is comparable to that of other methods of end-point indication and has

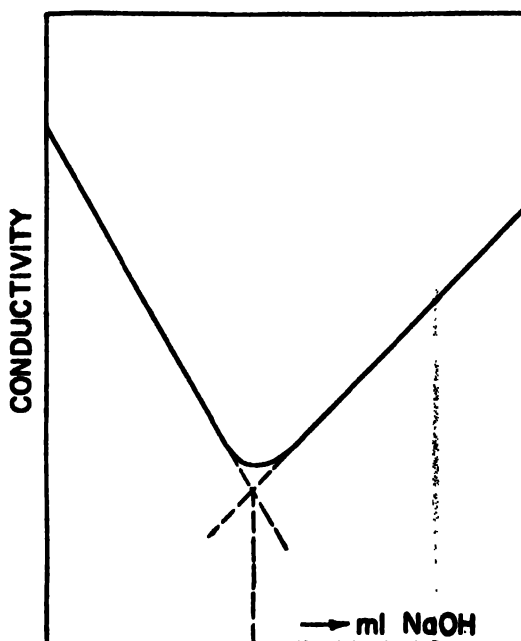


Fig. 1

the advantages of requiring simple apparatus, working in highly colored solutions and being very generally applicable. The disadvantages are the necessity for the reaction to be ionic, the failure of the method in cases where a high concentration of supporting electrolyte is present (e.g., sulfuric acid in a dichromate oxidation) and the requirement of plotting data as the reaction proceeds in order to find the end point.

F. R. DUKE

Cross-references: *Ions, Solutions, Analytical Chemistry*

COOLANTS

Coolants represent a general class of heat-transfer agents used in a flow system to convey heat from a source. The energy transfer from the source to the flowing or circulating medium is manifested most frequently as sensible heat, producing a temperature rise in the coolant. The magnitude of the coolant temperature rise, ΔT , is dependent upon the flowing heat capacity, wc (where w is the mass flow rate of coolant and c is the heat capacity of the coolant), and the rate of heat transfer, q , where in simple cases, $q = wc\Delta T$. In cases where the specific heat is a function of temperature and pressure, and/or where phase changes occur, reference should be made to the thermodynamic equations, charts and tables available for most common coolants for the evaluation of the coolant exit enthalpy and temperature rise. The ΔT is called the transport temperature rise. Properties of the coolant other than the specific heat may be utilized, such as latent heat associated with melting, vaporization, sublimation, or other phase transitions. Flow systems with endothermic reactions can also be adapted as coolants. By far the most common coolants are water and air, and involve energy transfer simply as sensible heat.

The transfer of energy as heat from a source to a coolant requires a temperature driving force designated as Δt , the transfer temperature rise. Factors which influence Δt include the heat-transfer coefficient of the coolant. The physical properties of the coolant affecting the heat-transfer coefficient are density ρ , heat capacity c , viscosity μ , thermal conductivity k , and in the case of natural convection, the coefficient of volumetric expansion β . The power expended for pumping the coolant may be a factor involving coolant selection, and the two important physical properties in the pressure drop and flow work evaluations are viscosity and density.

Aside from the usual requirements concerning availability and price, other coolant properties which need be considered are the phase pressure-temperature saturation curves, thermal stability, and component compatibility covering scale, corrosion, and in some high-temperature cases, metal transfer. The choice of coolant for special purposes, such as involved in nuclear reactors, requires the evaluations of neutron absorption cross-sections, of possible induced radioactivity,

and of radiation (exposure to fast neutron and gamma fluxes) damage. As an illustration, heavy water has more desirable nuclear properties than light water, and if its availability could be markedly improved and its price reduced, heavy water would find even more extensive use as a reactor coolant. Though gases, in comparison to liquids, have relatively poor heat-transfer characteristics, the extensive use of air, for example, is dependent largely on its no-cost basis. Other factors that can limit the choice of coolant in special applications, to note but a few, are the use of air rather than water as a coolant to render graphite-moderated, natural uranium reactors nonautocatalytic, the use of hydrogen in cooling electric generators because of its high specific heat and low windage loss, and the use of natural gas as a cooling and reducing medium. A very common example of a gas coolant acting also as a carrier is in water cooling towers with forced or natural draft. Some other special properties that have been emphasized include total weight of coolant system in airplane designs, and good wetting and spreading action in water emulsion cutting coolants, along with lubricity to produce a fine finish.

Low-temperature coolants include salt-water solutions, ethanol, methanol, glycols, glycerol; common industrial refrigerants such as ammonia, sulfur dioxide, the "Freons", methyl chloride, propane, butane, and propylene; and high-pressure refrigerants including methane, ethylene and carbon dioxide. Liquefied gases (air, nitrogen, hydrogen and helium) are used for very low temperature cooling.

Significant reductions in system operation pressures (and hence possible savings in equipment design) can be achieved by using coolants other than water for high temperature heat exchange. For example, up to temperatures in the range of 700°F, coolants used include oil, "Dowtherm" (eutectic mixture of 73.5% diphenyl oxide and 26.5% diphenyl), and mercury. For somewhat lower temperature limits, chlorinated biphenyl and tetraryl silicates can be used. Above 700°F, special inorganic salt mixtures have been used, such as HTS (40% NaNO_2 , 7% NaNO_3 and 53% (wt) KNO_3). The nuclear reactor program has accelerated the development of the technologies for handling molten metals, including sodium, sodium-potassium alloy (NaK), and bismuth. Other molten metals suggested as coolants include lead and lead-bismuth eutectic.

Solids may also be used to remove or transfer heat, and to stabilize temperature. For example, some designs of moving beds (pebbles of ceramic materials) represent significant improvements over the bulky regenerative type of heat exchange. In the catalytic cracking of petroleum, new developments are the giant fluidized beds. Elemental solids with high melting points and relatively high volumetric heat capacities have been proposed as coolants for high temperatures.

Safety is a dominant factor which cannot be overlooked in handling potentially hazardous coolants. For example, for handling liquid metals and radioactive coolants, many new techniques are emerging for obtaining leak-tight systems.

COMPARISON OF HEAT-TRANSFER FLUIDS FOR HIGH TEMPERATURES*

	Sodium	NaK (44% K)	HTS †	Dowtherm A ‡	Mercury	Lead	Pb-Bi Eutectic
Melting Point, °F	208	65	290	55	-37	622	257
Boiling point, °F							
14.7 psia	1616	1518	—	485	675	3170	3038
100 psia	—	—	—	690	908	—	—
500 psia	—	—	—	(940)	1194	—	—
Liquid Density							
g/cc at m.p.	.9287	—	1.97	—	—	10.2	—
60°F	—	.91	—	—	13.5	—	—
1000°F	—	.778	1.69	—	12.3	—	10.0
Specific Heat	.33-.30	0.28	.373	.63-.69	0.033	.034	.035
Btu/lb. °F				(Liquid) 500°-750°			290°-680°
Latent Heat of Vapor, Btu/lb.	1980	—	—	140.-89.	127	365	—
Thermal Conductivity (Btu) (ft) (hr) (°F) (ft²)	49-38	14-16	—	.105 400°-600°	5-9.	8.	5.3-6.5 320°-610°
Heat-Transfer coeffi- cient Btu (hr) (°F) (ft²)	6400 10 ft/sec	3500 10 ft/sec	200-2600 depend- ing on Vel. and Temp.	200-300 condens- ing	5700 10 ft/sec	4100 10 ft/sec	3700 10 ft/sec
Latent Heat of fusion Btu/lb.	49	—	35	—	—	11.3	—
Viscosity centipoise at m.p.	0.70	—	19.	5.	1.9	2.1	—
600°F	.30	0.24	2.9	0.35	—	—	1.75
1000°F	—	0.12	1.1	—	—	1.7	1.24
Probable Temperature range, °F	250-1500	100-1400	400-1000	360-750	-37-1000	650-1700	300-1700

* "Liquid Metals Handbook", 2nd Edition, 1952.

† Heat Transfer salt composed of NaNO_2 , NaNO_3 , and KNO_3 .

‡ Eutectic Mixture of diphenyl and diphenyl oxide.

Special designs are used in liquid metal-to-water heat exchangers to detect and prevent leakage.

HERBERT S. ISBN

Cross-references: *Heat Transfer*

COORDINATION COMPOUNDS, see CHELATION, SEQUESTERING AGENTS

COPPER & BRASS RESEARCH ASSOCIATION

The Copper & Brass Research Association is a trade association of the brass mills in this country. Brass mills roll, draw and form plate, sheet, strip, tube, pipe, rod, wire and shapes of copper, brass, bronze and other copper-base alloys containing 40% or more of copper. The brass mill industry also includes the forging of copper and its alloys but it does not include the producers of the raw metals, foundries, or the production of wire and cable for electrical transmission.

The Association was organized in 1921, and its primary purpose then was to help dispose of the large surplus of copper which had accumulated by the end of World War I and for which there was, at that time, little visible demand. In 1933 the so-called "Copper and Brass Mill Products Asso-

ciation" was formed by the brass mills to consider problems other than those for which the Research Association was formed. At a joint meeting on April 30, 1940 the two associations were merged under the name of the Copper & Brass Research Association.

The Association concerns itself with research, product promotion, publicity, technical problems, statistics, information, industrial relations, traffic and standards. It has standing committees consisting of properly qualified representatives from the Industry which, in frequent meetings, plan its activities in these various fields. The work of these committees is coordinated through an Executive Committee responsible directly to the Board of Directors. The Board consists of a group of executives, representative of the Industry as a whole, and it, with the advice of legal counsel, makes the final determination as to the propriety and desirability of all work carried on by the Association. The execution of the work which has been approved as an Association undertaking is the responsibility of the Manager, who is the operating executive of the Association, and his staff.

From a technical viewpoint the two important activities of the Association have to do with re-

search and standardization. Its Technical Committee reviews the problems having to do with the manufacture and utilization of the various mill products, and where the need is indicated initiates research projects to seek the answers to the problems. The Association has no laboratory of its own, and the procedure generally follows one of three courses. A sponsored research project may be arranged at a college, university or other institution specially equipped for and interested in the problem at hand. An alternative for certain types of problems is to refer the proposition to the laboratories of the various brass mills, basing the report on the consensus of the findings. If the problem is a relatively minor one, it may be referred to the laboratory of just one company.

The Committee on Standards has been engaged for about twenty years in an extensive and intensive development of comprehensive standards applicable to brass mill products. These standards, using the term "standards" in its broader sense, are compiled in a so-called "Manual of Standards" listing useful information, including physical and chemical characteristics, pertaining to about forty of the more commonly used copper-base alloys. Included also are standard dimensional and related tolerances for all the principal brass mill products, terminology applicable to the products of the Industry, weight tables and other estimating data. The standard tolerances are broadly representative of good mill practice and are indicative of what the purchaser may expect under normal commercial conditions where particular tolerances are not specified by them. The wide circulation of the Manual of Standards is among users of the products of the Industry, and has served to provide information which it is believed they need for a better practical understanding of brass mill products.

The Association is a member of the American Standards Association and is represented not only on the Council and in the Conferences of Executives of Organization Members, but also on sectional committees whose work has any bearing on the products of the Industry. Together with other interested groups it has been and is active in the development of many complete standards, including the acceptance as ASA standards of the standards developed for the Manual of Standards. In addition to this cooperation with ASA, the Association through its association with and representation in such groups as the American Society for Testing Materials, the American Society of Mechanical Engineers, the Society of Automotive Engineers and others, has assured that the standards are not only representative of good mill practice, but also meet the needs of the users of the materials of the Industry. Every attempt is made by the Association to keep these standards strictly up-to-date and thus reflect the latest developments in mill practice. By working closely with the other specification-writing bodies, including various government agencies, much has been accomplished to eliminate, as far as practical, inconsistent and ambiguous requirements in the various specifications covering brass mill products.

Not the least of the standardization has been to define what is meant by copper, brass and bronze, and it should be pointed out that in discussing brass mill products, all of the coppers, brasses and bronzes are included.

T. E. VELTFOOT

Cross-references: Copper, Metals

COPPER AND ITS COMPOUNDS

Metallic Copper

Copper, the leading nonferrous metal, has been used since prehistoric times, and is used today in greater amounts than ever before. Its combination of high electrical and thermal conductivity, resistance to corrosion, ductility, and suitable strength, as well as its many valuable alloys, make it an extremely useful metal.

Occurrence. Copper is widely distributed in many parts of the world, and is found in a variety of ore minerals. The ores, however, are for the most part of low grade. Higher-grade ores once available have been exhausted, and those being mined at present in the United States average less than one percent copper. The ores are classified in three groups: sulfide, oxidized, and native copper. The sulfide ores are by far the most important. Chief among the sulfide minerals are chalcocite, Cu_2S , and chalcophyrite, CuFeS_2 . Other principal minerals in this group are covellite, CuS ; bornite, Cu_5FeS_4 ; enargite, $\text{Cu}_3(\text{As}, \text{Sb})\text{S}_4$; tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$; and tennantite, $\text{Cu}_{12}\text{As}_4\text{S}_{13}$. The oxidized ores include the copper oxides and combinations of these with CO_2 , SO_3 , SiO_2 , and H_2O . Native copper ores, containing uncombined copper, at one time occurred in numerous localities, but now are found in commercial tonnages only in the State of Michigan.

Many of the large low-grade copper ore bodies have the copper minerals disseminated in small particles through monzonitic igneous rock called "porphyry". The disseminated minerals are usually sulfides, sometimes oxides. Over 40% of the world's copper supply is currently coming from porphyry deposits, which include the leading deposits of the western and southwestern United States as well as in other countries. The sulfide copper ores, and sometimes others, usually contain gold and silver in important amounts; the recovery of these metals is effected through electrolytic refining of copper.

Production. The world's production of new (primary) copper in 1953 was a little over 3,000,000 short tons. The leading countries were: United States, with 31% of the total production; Northern Rhodesia, 13%; Chile, 13%; Russia, 11% (estimated), Canada, 8%; Belgian Congo, 8%. The American Bureau of Metal Statistics, which is the source of the data quoted, lists production from 28 other countries, no one of which contributed as much as 2.5%. Of the 925,000 tons produced from United States mines, 42% came from Arizona, 29% from Utah, 9% from Montana, 7% from New Mexico, 7% from Nevada, 3% from Michigan, and 3% from other states.

In addition to the above production of primary

copper, there is a large output of secondary or scrap copper. In the United States this amounted to 941,000 short tons in 1953, of which 409,000 tons was old (used) scrap and 532,000 tons was new (manufacturing) scrap. These figures include the copper content of scrap brass and other copper alloy scrap.

Extraction from Ore. Copper may be extracted from its ores either by smelting or by leaching, but more than nine-tenths is obtained by smelting. Before furnace treatment the ores are concentrated by the flotation process with preliminary fine grinding and classifying. This yields concentrates commonly carrying 15 to 50% copper. Except in a few instances the ores are not smelted directly to metallic copper, but are smelted to matte, which is composed essentially of copper sulfide (Cu_2S) and iron sulfide (FeS), together with lesser amounts of other sulfides and Fe_3O_4 . It is necessary to control the copper content of the matte, and this is done by adjusting the amount of sulfur in the charge by mixing different ores and often by preliminary roasting to eliminate part of the sulfur. Smelting is usually done in large reverberatory furnaces fired with natural gas, oil, or pulverized coal. Modern furnaces usually have a capacity between 700 and 2,000 tons of charge per 24 hours. Silica and other oxide constituents either existing in the charge or formed in the furnace combine with added flux to form a slag. The principal flux is iron oxide, usually with a small amount of limestone, forming a slag that is primarily a silicate of iron and some lime.

In order to obtain metallic copper from matte, the latter is transferred to a converter while still molten, where it undergoes an operation analogous to the Bessemer steel process. Air is blown through the matte, oxidizing the iron and sulfur; the latter passes into the gas as sulfur dioxide, while the former is slagged by addition of silica as a flux. Copper 98 to 99% pure, called "blister copper," remains. The converter, in the shape of a horizontal barrel, may produce about 75 tons of blister copper in a 12-hour blow, the production and time depending upon the grade of the matte. No fuel is used, the necessary heat being derived from oxidation of iron and sulfur.

In the hydrometallurgical method of extraction, the ore is leached without prior concentration, usually with sulfuric acid. The copper is extracted from the resulting solution either by electrolysis or by cementation on iron. The electrolytic method regenerates the acid and the solution is used again for leaching.

Refining. Specifications for copper for electrical uses call for a minimum purity of 99.92%. Electrolytic refining is required to achieve this standard, as well as to recover gold and silver present in the ore and which remain in solution in the matte and blister copper. The preparation of anodes suitable for electrolytic refining necessitates a preliminary furnace refining, which is essentially a process of oxidizing those impurities more readily oxidized than copper. The anodes are suspended in an electrolyte of copper sulfate and sulfuric acid. Copper of 99.98% purity is deposited on the cathodes, which are

usually remelted and cast into wire-bars, cakes, billets, and other shapes suitable for rolling, drawing, extrusion, and other fabricating methods. Some of the impurities contained in the anodes dissolve in the electrolyte without plating out at the cathode, while others remain insoluble at the anode. The latter, constituting the "anode slime", include the gold and silver, which are recovered by further treatment of the slime.

Chemistry and Properties. Copper is the first element of subgroup IB of the Periodic Table. Its atomic number is 29 and the electron configuration is 2:8:18:1. The crystalline structure is face-centered cubic, with the cube side dimension $a = 3.6080 \text{ kX}$ at 20°C . The minimum interatomic distance is 2.551 kX .

The density of copper is 8.94 at 20°C , while that of liquid copper at the melting point is 7.93 . The melting point is 1083°C and the normal boiling point about 2595°C .

The atomic weight of copper is 63.54 . The natural element is a mixture of the two isotopes Cu^{63} , with 29 protons and 34 neutrons, and Cu^{65} , with 29 protons and 36 neutrons. Unstable isotopes of mass numbers 60, 61, 62, 64, 66, and 67 have been found; of these Cu^{67} has the longest half life, 56 hours.

The electrical conductivity of copper is commonly stated in terms of a standard adopted by the International Electrotechnical Commission, which assigns a percentage value of 100 to copper having a mass resistivity of $0.15328 \text{ ohm (meter, gram) at } 20^\circ\text{C}$. This value, called the International Annealed Copper Standard (IACS), corresponds to a volumetric resistivity of 0.0000017241 ohm for a cube measuring 1 cm on each side.

Specifications require that copper for electrical use meet the IACS conductivity of 100, but pure copper (polycrystalline) has been made having a conductivity of 102.3, and most commercial copper falls between 100.5 and 101.8. The volumetric conductivity is 94% of that of silver, while that of the next highest metal, gold, is only 66% of that of silver. The thermal conductivity at 20°C is $0.934 \text{ cal per sq cm per cm thickness per } ^\circ\text{C per sec}$.

The heat of fusion of copper is $48.9 \text{ cal per gram}$ and the heat of vaporization about $1150 \text{ cal per gram}$. The specific heat of the solid is $0.092 \text{ cal per gram at } 20^\circ\text{C}$ and increases between 0 and $t^\circ\text{C}$ according to the expression $0.092 + 0.0000250t$ cal per gram. The specific heat of the liquid is 0.112 and of the vapor approximately 0.08 . Copper is diamagnetic, having a susceptibility of $-0.080 \times 10^{-6} \text{ cgs units per gram at } 18^\circ\text{C}$.

The ultimate tensile strength of hot-rolled copper is about $32,000 \text{ psi}$, yield strength $19,000 \text{ psi}$, elongation 45 to 55% in 2 inches. The tensile strength of cold-worked copper increases to about $57,000 \text{ psi}$ after 70% reduction in area, with decrease of elongation to 4%. The elastic modulus in tension is $17,000,000 \text{ psi}$ for annealed copper.

The mechanical properties stated above are those of electrolytic tough-pitch copper, which is purposely cast with an oxygen content of 0.03 to 0.04%. Some commercial copper is sold as oxygen-free copper; some of the properties of this form will differ slightly from those of tough-pitch copper.

The standard potential of bivalent copper is +0.34 volt at 25°C. Its excellent corrosion resistance is due both to its relative nobility in the electropotential series of metals and to the formation of a protective film. In weathering, the coating is composed of hydrated copper carbonate, which is mixed with basic copper sulfate in industrial atmospheres. The coating is green and while somewhat powdery at the surface is dense and adherent at the junction with the underlying metal. Under other conditions, and especially when heated, copper receives a coating of black oxide, CuO , when freely oxidized, or of brilliant purplish red Cu_2O when oxidation is restrained, as by spraying with water while hot.

Uses. About 55% of the usage of copper is for electrical purposes, including power transmission and generation, telephone and telegraph, motors, switchboards, lighting, radio and television, air conditioning, electric refrigerators and clocks, electric wiring, etc. About 15% is used in building construction, including pipes and plumbing, roofing, gutters, leaders, hardware, etc. The automotive industry takes about 12%, not including the electrical parts. Machinery and industrial equipment consumes 9%. These figures include the copper contained in brass and other alloys as well as pure copper. In time of war the use of copper in cartridge cases, shell bands, etc., as well as for field communications and in ships, tanks, and trucks, is greatly augmented.

Copper Alloys

A notable feature of copper is the number, variety, and usefulness of its alloys. The principal classes of alloys with respect to composition are as follows:

- Copper-zinc (binary brasses)
- Copper-tin (binary bronzes)
- Copper-zinc-tin (special brasses and bronzes)
- Copper-zinc-lead and copper-tin-zinc-lead (leaded brasses and bronzes)
- Copper-zinc-nickel (nickel silvers)
- Copper-zinc-manganese plus tin, iron, aluminum (manganese bronzes)
- Copper-tin-phosphorus (phosphor bronze)
- Copper-aluminum and copper-aluminum plus iron, nickel, or manganese (aluminum bronzes)
- Copper-silicon plus manganese, tin, iron, or zinc (silicon bronzes)
- Copper-nickel (cupronickel)
- Copper-beryllium and copper-cobalt-beryllium (beryllium copper)

Copper alloys are classified as the wrought alloys and the casting alloys. The wrought alloys are for the most part compositionally simpler, including a number of binary alloys. Several of the important casting alloys contain both zinc and tin and in many cases lead also. Most of the alloys which do not contain lead are difficult to machine, and lead may be added to many of the alloys to improve their machinability.

Brass is designated according to zinc content as *low brass* (up to 20% zinc) and *high brass* (30% zinc and above). It is also designated as *red brass* (up to 20% zinc) and *yellow brass* (30% zinc or

more). These terms are also applied to specific compositions. The copper-zinc equilibrium diagram shows that zinc forms a face-centered solid solution with copper up to about 39% zinc. This constitutes "alpha brass". From 39 to 46% zinc a body-centered solid solution, beta, occurs with the alpha constituent. Since equilibrium is not reached under ordinary conditions, the beta constituent may be found in compositions as low as 35% zinc. Alpha brass is harder and stronger than pure copper, and its ductility also increases progressively, reaching a maximum at 30 per cent zinc; brass of this composition is named *cartridge brass*.

Hardness and strength reach a maximum at about 40 per cent zinc, brass of this composition being known as *Muntz metal*. Brass containing more than 40% zinc are rarely used owing to decreasing ductility and lowered corrosion resistance.

Copper Compounds

Copper forms both cuprous (Cu^+) and cupric (Cu^{++}) compounds; and Cu^{1+2} occurs in a few unstable compounds. Among the more important cuprous compounds are *cuprous cyanide*, CuCN , which is used in the double-cyanide electroplating baths and as a catalyst for various organic reactions; *cuprous chloride*, CuCl , which has many catalytic applications; and *cuprous oxide*, Cu_2O , used in rectifiers and as a fungicide.

Important cupric compounds are more numerous. The sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is the leading industrial copper compound. It has extensive agricultural applications as a fungicide and as a soil additive to prevent copper deficiencies in crops or animals or improve crop yields. It forms the copper plating bath of largest use and has many minor applications. Direct use as a fungicide has decreased greatly, but it is used to prepare other fungicides. Mixed with lime it forms *Bordeaux mixture*, the reaction on mixing forming $\text{Cu}(\text{OH})_2$ and CaSO_4 ; this mixture is used to control plant diseases in many crops. Cupric arsenite, *Paris green*, approximating the composition $(\text{CH}_3\text{COO})_2\text{Cu} \cdot 3\text{Cu}(\text{AsO}_2)_2$, and cupric arsenite, *Scheele's green* (variable composition), are used as wood preservatives and as larvicides for mosquito control. They were formerly used as pigments and insecticides.

Basic cupric carbonates and cupric oxide, CuO , are used as coloring agents, and the former also for their insecticidal and fungicidal properties. *Cupric chloride*, CuCl_2 , is employed as a catalyst, as a deodorizing and desulfurizing agent in petroleum refining, and for many other purposes.

A number of organic copper compounds are in use. The most important is *copper naphthenate*. It is used for preservation of fish nets and fabrics exposed to weathering, as a wood and fabric preservative, in sterilizing wells, and its use as a fungicide is being developed.

ALLISON BUTTS

Biochemical Behavior of Copper

Plants. The activity of copper in plant metabolism manifests itself in two forms: synthesis of

chlorophyll and activity of enzymes. In leaves, most of the copper occurs in close association with chlorophyll, but little is known of its role in chlorophyll synthesis, other than that the presence of copper is required.

Copper is a definite constituent of three enzymes catalyzing oxidation-reduction reactions (oxidases), in which the activity is believed to be due to the shuttling of copper between the +1 and +2 oxidation states. Ascorbic acid oxidase catalyzes the reaction between oxygen and ascorbic acid to give dehydroascorbic acid. This oxidase occurs widely in plants, particularly in cucurbits and beans, yet it is not known how it fits into the overall metabolism of the plant. Tyrosinase, also known as polyphenol oxidase or catechol oxidase, occurs in potatoes, spinach, mushrooms, and other plants. It catalyzes the air oxidation of monophenols to ortho diphenols, and the oxidation of catechol to dark-colored compounds known as *melanins*.

Traces of copper are required for the growth and reproduction of lower plant forms, such as algae and fungi, although larger amounts are toxic.

The effects of copper deficiency in plants are varied and include: die-back, inability to produce seed, chlorosis, and reduced photosynthetic activity. On the other hand, excesses of copper in the soil are toxic, as is the application of soluble copper salts to foliage. It is for this reason that copper fungicides are formulated with a relatively insoluble copper compound. These compounds, usually insoluble basic salts which are harmless to most plants, are still sufficiently soluble to be toxic to fungi.

Animals. The body of the adult human contains 100-150 mg of copper, the greatest concentrations existing in the liver and bones. Blood contains a number of copper proteins, one of which, globinioxidase, appears to catalyze the oxygenation of hemoglobin in the lungs. Copper is known to be necessary for the synthesis of hemoglobin, although there is no copper in the hemoglobin molecule. Anemia can be induced in animals on a low copper diet, such as milk, whereupon iron is assimilated but is merely stored in the liver, and is not converted into hemoglobin.

Copper is also required for the synthesis of a number of enzymes, and is involved in the glycolysis or breakdown of sugars.

The blue copper protein hemocyanin occurs in the blood of certain lower forms of animal life. This compound performs the oxygen-carrying function for these species. This protein is believed to be a polypeptide containing +1 copper. It is not, however, as efficient an oxygen carrier as hemoglobin. Like the copper enzymes, hemocyanin is inactivated by cyanide, but can be reactivated by treatment with soluble copper salts. The enzyme tyrosinase is found in many animals, being mainly responsible for skin pigmentation and for hardening of fresh tissue in molting species.

Copper is also found in bacteria; in the diphtheria bacillus copper is necessary for the production of toxins.

Anemia induced by a low-copper diet is rare in human adults because of the widespread occurrence of copper in foods. In some places, e.g. Australia and Holland, diseases of cattle and sheep, involving diarrhea, anemia and nervous disorders, can be traced either to a lack of copper in the diet, or to excessive amounts of molybdenum, which inhibits the storage of copper in the liver.

Ingestion of copper sulfate by humans causes vomiting, cramps, convulsions, and as little as 27 g. of the compound may cause death. An important part of the toxicity of copper to both plants and animals is probably due to its combination with thiol groups of certain enzymes, thereby inactivating them. The effects of chronic exposure to copper in animals are cirrhosis of the liver, failure of growth, and jaundice.

R. R. GRINSTEAD

Cross-references: *Metals, Corrosion, Chlorophyll*

CORN INDUSTRIES RESEARCH FOUNDATION

Corn Industries Research Foundation, Inc., is an organization formed by the corn wet-milling industry, which processes the corn kernel by means of chemically treated water to obtain starch, gluten and oil, combining much of the by-product residues into animal feeds. Some companies in this industry convert part of their starch output to corn syrup and dextrose (corn sugar). Other more specialized products are zein, which is used to make protein fibers, and other materials such as amino acids and monosodium glutamate.

Incorporated under the laws of the State of Indiana, the Foundation is an evolutionary outgrowth of the American Manufacturers Association of Products From Corn, established in March, 1913, and its successor, the Associated Corn Products Manufacturers, organized in 1923. The latter was in existence until 1932, when the need for scientific and other research became apparent and the Corn Industries Research Foundation was organized. Its present members are: American Maize-Products Company, Anheuser-Busch, Inc., Clinton Foods Inc., Corn Products Refining Company, The Hubinger Company, The Huron Milling Company, The Keever Starch Company, National Starch Products, Inc., Penick & Ford, Limited, Inc., A. E. Staley Manufacturing Company, and the Union Starch & Refining Company.

Governing body of the Foundation is the Board of Trustees, made up of one top executive (usually the president or chairman of the board) from each corporate member—eleven in all. A president and a vice-president are elected from the trustees, serving in voluntary capacities. Other officers are staff employees, including an executive vice-president, a vice president, secretary and treasurer, director of research and editorial director.

Basic policies governing the Foundation's various activities are under the jurisdiction of several standing committees which at present include the executive committee, the finance committee, the research committee and the public relations committee.

The main emphasis in the Foundation's research program is on basic or fundamental research. Since the Foundation has no facilities of its own suitable for fundamental research, these activities are carried on in university, government and (in a few instances) private research institutes. The Foundation endeavors to establish projects in the general areas of industry interest, largely at present in the field of carbohydrate chemistry with special emphasis on starch, since starch makes up a large proportion of the corn kernel.

All approaches to the problem of corn chemistry are cultivated, and an attempt is made at cross-fertilization of many special approaches. To coordinate all these approaches the now well-known Starch Round Table was organized where carbohydrate research specialists from government, university and industrial laboratories meet for five days once a year to review progress in the field. The conference has been held annually for fifteen years and has immeasurably speeded up general advances in starch chemistry.

Offices of the Foundation are located at 1001 Connecticut Ave. N.W., Washington, D. C.

NORMAN F. KENNEDY

Cross-references: *Carbohydrates*

CORROSION

Corrosion is defined as the destructive alteration of a metal by reaction with its environment. Its economic importance is indicated by estimates that the annual cost of corrosion due to losses that result from it and the expenses of preventing it amounts to at least \$6,000,000,000 per year for the world at large.

The basic cause of corrosion and the force that drives it is the difference in free energy between refined metals and the ores from which they have been derived or the compounds which they form during the processes of corrosion; the latter frequently are the same as the former. This is illustrated by iron where the oxides (ore) from which it is refined are almost identical in composition with the rusts formed by corrosion. The processes of corrosion, therefore, represent a retreat of the refined metals to their original compounds.

In corroding, metals become ionized and acquire positive electrical charges in accordance with the valence forces involved. Differences in potential and flow of current between discrete areas on a single metal surface or between dissimilar metals in a corrosive environment can be measured. There is ample evidence in support of the theory that corrosion is essentially an electrochemical process. This involves the presence of an anode where current leaves the metal, a cathode where current enters the metal, an electrolyte to conduct the ionic current between these anodes and cathodes, and a metallic or semimetallic path to conduct the electrons in that portion of the circuit which is outside the electrolyte.

The free energy relationships between most metals and their possible corrosion products are such that, in most cases, corrosion reactions should be spontaneous and proceed at high rates.

Fortunately, however, these possible rates of reaction are reduced greatly by opposing influences, such as the formation of adherent corrosion products which are insoluble in the environment in which they are formed or in others that may be encountered subsequently. These serve as a barrier, and establish rates of further attack that are determined by the relatively low rates of diffusion of metal through the corrosion product to the corroding liquid or vice versa. This is exemplified by aluminum which should corrode at a high rate in moist air, but which is prevented from doing so by the formation of a protective film of aluminum oxide. Much thinner films involving oxygen are responsible for the phenomenon of passivity exhibited academically by iron after immersion in concentrated nitric acid and practically by chromium and the high chromium iron and iron-nickel alloys known as the stainless steels. Protective oxides and passivity are most important in determining the corrosion resistance of metals and alloys made from them that are listed above hydrogen in the standard electromotive series. Those that lie below hydrogen, e.g. copper, are less dependent on passivity for corrosion resistance.

The relationships between metals and hydrogen in the electromotive series are important because in the electrochemical processes of corrosion the discharge of hydrogen ions and the evolution of hydrogen as a gas is one of the principal cathodic reactions. The facility with which this can occur is determined by such factors as the hydrogen ion concentration (pH) of the electrolyte, the electrical potential of the corrosion cell, and the over-voltage characteristics of the cathodic surface.

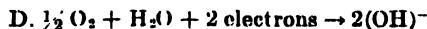
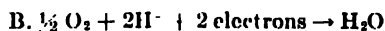
Hydrogen evolution is not the only possible cathodic reaction; others include a possible reaction between atomic hydrogen and dissolved oxygen or, more likely, the direct reduction of oxygen in water to form hydrogen peroxide as a first step, or hydroxyl ions as a final product.

Thus, the electrochemical reactions in corrosion of a divalent metal may be written:

Anodic reaction



At the cathode



It is evident that oxygen as well as hydrogen plays an important part in corrosion. It can accelerate corrosion by participating in cathodic reactions, or it can retard corrosion by forming protective oxides or passive films. This dual effect of oxygen is one of the things that complicate corrosion processes, the interpretation of observations and the steps to be taken to avoid corrosion difficulties.

Forms of Corrosion. (1) Pitting resulting from local action currents, as at discontinuities in protective or passive films or under or around deposits

that set up concentration cells. (2) Stress corrosion cracking resulting from the combined effects of corrosion by a specific environment and either applied or internal static tensile stresses; depending on the metal and the environment the cracks may be either intercrystalline or transcrystalline. (3) Corrosion fatigue, resulting from the combined effects of corrosion and cyclic stresses; these cracks are characteristically transcrystalline. (4) Intergranular corrosion resulting from preferential attack on, or around, a phase or compound that occupies grain boundaries. (5) Erosion resulting from the combined effects of corrosion and either abrasion or attrition. The mechanism usually involves local or general removal of otherwise protective corrosion product films. Particular forms are impingement attack due to effects of high velocity or turbulence in flowing liquids, e.g., salt water in steam condensers or other heat exchangers, in piping systems, valves, pumps, etc. A particularly aggressive form is associated with the severe mechanical forces that are characteristic of cavitation phenomena. (6) Uniform attack or general wastage, such as may be caused by the action of strong acids as used for pickling (scale removal) or etching. This is also characteristic of the slow corrosion of durable materials in appropriate environments, such as copper roofs in suburban atmospheres, cupro nickel tubes in ships condensers, Monel—nickel copper alloy—racks for pickling steel in sulfuric acid, or stainless steel columns handling nitric acid.

Preventive Measures. (1) Use of the right metal in the right way in the right place. (2) Protective coatings—paints, enamels, other metals, oils, greases, etc. (3) Inhibitors, i.e., compounds added to the environment in small concentrations to form protective films which increase anodic or cathodic polarization, or both, or neutralize some corrosive constituents. (4) Neutralizing agents added to adjust acidity or alkalinity to a desired level. (5) Removal of dissolved oxygen or other corrosive gases by 'deaerators' or the addition of chemicals to react with oxygen (oxygen scavengers). (6) Drying of air or other gases to keep humidity below level where corrosion can occur. (7) Design of hydraulic systems to avoid excessive velocities or localized turbulence or to maintain a velocity high enough to prevent the accumulation of corrosion products or other deposits that would promote localized corrosion. (8) Various features of design and operation of structures or equipment to favor rapid drainage and drying, prevent accumulation or concentration of corrosive chemicals in crevices or low spots, hold operating stresses and temperatures within desired limits, eliminate fabricating stresses by appropriate heat treatment, avoid galvanically unfavorable combinations of different metals, provide protection against stray electrical currents by appropriate insulation and electrical bonding. (9) Heat-treating metals to leave them in optimum condition to resist corrosion. (10) Applying protective electrical currents (cathodic protection) from sacrificial metals (galvanic anodes) such as zinc, magnesium or aluminum or from some external source through a graphite, platinum or other appropriate

anode receiving current from a rectifier, generator, or battery. The location of the anodes, the magnitude of the current and the applied voltage must be engineered so that without wasting current all surfaces that require protection will receive enough current to achieve this effect. Too much current may cause damage by the alkali generated by a cathodic reaction or by hydrogen evolved at the cathode which can destroy protective films or embrittle metals.

Continued research, especially of a fundamental kind, is necessary to learn more about the basic nature of corrosion as a guide to better alloys, better testing methods, better interpretation of data and improved means of preventing corrosion.

FRANK L. LAQUE

Cross-references: Metals, Electrochemistry, Electromotive Series, Exposure Testing

COSMETICS

Cosmetics are preparations applied to the surface of the body for the purpose of enhancing its appearance. They may be (1) make-up preparations, applied to bring about temporary effects, lasting only so long as the preparations remain on the body surface, or (2) treatment preparations, which effect no immediately noticeable change but which after repeated use are expected to have a beautifying effect.

The skin, on its outer surface, is an inert, rather tough material well suited to protect the delicate inner tissues from injury. The dead cells forming the outer layers are hard, rather dry, and expendable. In deeper layers of the skin, the cells are softer, alive, and vulnerable. An essential characteristic of the living cells forming the inner layer of the epidermis is their ability to divide and produce new cells which continually push the older cells upward. These older cells gradually toughen as soft proteins are changed to hard, horny keratin.

The living cells of the inner epidermal layer are believed to contain "tonofibrils" of composition similar to keratin, which may serve as crystallization centers for deposition of more keratin which is formed from the globular proteins of the cytoplasm as the cell ages and dies. This transformation of protein may be considered a denaturation process, with the long coiled chains of the globular proteins unfolding and assembling into the parallel bundles found in keratin.

Keratins are fibrous proteins, insoluble and relatively inert to chemical agents. The lengths of the molecules are over 100 times their thickness. Bundles of such molecules form fibers. In hair, the long axes of the keratin molecules lie roughly parallel to that of the hair; in nails, the fibers run transversely; in epidermal cells they run in all directions. Molecules are held together in the fibers (1) by linkage of the SH groups of their cystein residues to form common, disulfide bonds; (2) by salt linkages between free carboxyl groups of one molecule and free amino groups of another; and (3) by hydrogen bonds between NH groups of

one molecule and CO groups of another. These linkages must be broken if the keratin is to be softened or altered.

Under the epidermis, the dermis contains blood vessels, lymph spaces, nerve endings, sebaceous and sweat glands, hairs in their follicles, and erector muscles for the hairs, all distributed in a matrix of connective tissue. This connective tissue contains a network of fibrous proteins (collagen, reticulin, elastin) filled in with a ground substance which appears to be semi-sol, semi-gel. Collagen, forming about 72% of the weight of dried, fat-free skin, has a high content of glycine, proline, and hydroxyproline; very low tyrosine, methionine, and histidine; and no cystine or tryptophan. Its molecular weight is about 10 million. Carbohydrates are intimately associated with collagen, in the proportion of two molecules of glucose and two of galactose to one molecule of chondroitin sulfate. Other mucopolysaccharides are present, probably bound to proteins. The structural unit of the collagen fiber is the microscopic fibril of diameter 0.3 to 0.5 micron. The fibers are bundles of these microfibrils. Reticulin fibers are branched, and are found mostly at the boundaries of the connective tissue. Collagen and reticulin fibers can be regenerated by living organisms, but elastin cannot. Elastin differs from collagen principally in having more alanine and valine, and less glutamic acid and hydroxyproline.

The skin contains varying amounts of fat, depending upon nutritional conditions. Intercellular depositions of glycerides (fuel reservoirs) are very variable; intracellular lipides (mostly sterols and phospholipides) are more constant.

It is a well-known fact that the skin of elderly persons is generally wrinkled, dry, and in general less attractive than that of younger individuals. Some of the changes taking place as skin ages are: (1) components become less highly hydrated; (2) cholesterol content decreases; (3) calcium content increases; (4) fat content decreases; (5) globular proteins decrease; (6) phospholipide content decreases; (7) sebum excretion drops (in women only); (8) tension and elasticity decrease; (9) tensile strength increases.

Treatment cosmetics, if they are to be effective, should be designed to prevent, counteract, or compensate for one or more of the above changes.

If cosmetic preparations are to influence the living cells in the deeper layers of the skin, and possibly in the subcutaneous tissues, they must be able to reach those cells. The horny layer presents a barrier to such penetration, but not one which is insuperable. Knowledge of the composition and properties of the skin makes it possible to select cosmetic ingredients which will promote absorption. Oils and oil-soluble substances are absorbed principally by way of the sebaceous glands. Selection of solvent, or of emulsion type, can have an important effect upon extent of absorption.

Cosmetic make-up is generally designed to impart a desired color or texture to some part of the body surface. The skin of the face may be powdered to reduce gloss, or covered with a more adherent make-up which remains fixed all day. Face

powders contain white pigments with high covering power, such as zinc oxide and titanium dioxide; colored pigments such as iron oxides; ingredients to give desired slip, such as talc; and materials to improve adhesion to skin, such as zinc stearate. In the more lasting make-up, the pigments are mixed with oils, waxes, etc., to improve adherence.

Rouge for the cheeks is similar to face powder, but contains bright red lakes of organic dyes in high enough concentration to redden the skin noticeably. Rouge for the lips is almost always prepared in the form of lipsticks, which have a base composed of wax and oil in such proportions as to remain stiff in hot weather but to be applied easily to the lips. Beeswax, carnauba wax, amorphous hydrocarbon waxes, castor oil, lanolin, butyl stearate, and polyethylene glycol and its esters are among the commonly used ingredients of lipsticks.

Nail "polishes" are generally colored lacquers with a nitrocellulose base. They are more lasting than most make-up preparations for the skin, and may stay on the nail until growth exposes a noticeable expanse of uncovered nail, necessitating removal and reapplication of the lacquer.

For all cosmetic preparations, ingredients must be free of any irritating or injurious effect under conditions of use. The U. S. Government has taken notice of the need for standardized coloring materials by providing that all coal-tar dyes for use in foods, drugs, and cosmetics must be certified by the U. S. Food and Drug Administration as harmless and suitable for such use. Manufacturers of cosmetic colors must submit to Washington a sample of each batch manufactured, and must obtain a certificate that the sample tested there was found to be composed of a dye on the approved list, and contained impurities in quantities below the specified limits. A certification number is assigned to each batch, and must be shown on the label of each container of color shipped to a cosmetics manufacturer.

For dyeing hair, phenylene diamine and similar compounds are much used. These amines are allowed to penetrate into the hair shaft; then an oxidizing agent is applied which converts the amine to a colored, insoluble compound which remains in the hair.

Bleaching of the skin with weak acids such as buttermilk and lemon juice has been practiced for centuries but is not very effective. Creams containing mercury salts, generally ammoniated mercury, are claimed to be effective bleaches, but their use involves some danger, and the mercury content is held to a low level by law. The mercury probably inhibits one of the enzymes involved in the production of melanin, the black pigment of the skin, from tyrosine. Hair is commonly bleached by hydrogen peroxide.

Since hair is a dead tissue, it may be subjected to rather drastic treatment. The salt links and disulfide links between adjacent keratin molecules may be broken by use of alkaline solutions of various sulfur compounds. Metallic sulfides are not convenient to use, but the ammonium salt of thioglycolic acid is well adapted to such application. The hair is wound on spindles, soaked with

the thioglycollate solution until it is made soft and nonelastic, then rinsed or oxidized until all excess thioglycollate is removed. The disulfide bonds are supposedly reformed at new positions so that the restiffened hair thereafter retains its imposed spiral shape.

The same agents that soften hair may be used in greater strength to remove unwanted hair. Metallic sulfides were once used, but have been largely replaced by ammonium thioglycollate, which is less irritating and gives off a less objectionable odor.

In addition to improving visual appearance, cosmetic preparations may be designed to enhance olfactory attractiveness. Most cosmetics are perfumed attractively by addition of odorants, but deodorants and perfumes are specifically intended for odor improvement. Deodorants must counteract the tendency of sweat and sebum to form ill-smelling materials on the skin. They may do this either by inhibiting perspiration or by preventing bacterial decomposition of the excreted products upon the skin. Antiperspirants generally contain aluminum salts which exert astringent action. The antibacterial deodorants contain germicides, such as hexachlorophene, which cling to the skin and inhibit bacterial action for long periods.

The deodorant properties of chlorophyllins have been the subject of much controversy. It appears that they are able to neutralize or destroy some odorants by adsorption of both a physical and a chemical nature.

Reference was made above to the changes occurring in the skin as an individual grows older. Treatment cosmetics are designed to prevent, counteract, lessen, or compensate for, the effects upon the skin of age and other damaging agents. Knowledge of the biochemistry of the skin is fragmentary, and we do not yet know how to make completely effective treatment cosmetics.

Creams containing suitable oils have long been used to counteract the dryness (lack of oil) attendant upon age. Among the most effective agents for increasing hydration of skin cells are the sex hormones and related steroids; their skin-hydrating effect has recently been found to be independent of their sex activity. These steroids are reported to make senile skin plumper and firmer, and thus to make it look younger. The treatment problem is largely one of stimulating the cells of skin and underlying tissues, so that they will be more active and behave more like younger cells.

New chemical products with potential application in cosmetics are appearing rapidly. They include solvents, surfactants, germicides, hormones, and substances of many other classes. They increase tremendously the range of effectiveness to be reached by the cosmetic chemist. Their actual use in cosmetics must be preceded by careful tests for safety, first on animals, then by patch tests on humans, and finally under actual conditions of proposed use. By such a procedure preparations that are safe and harmless, as well as effective and attractive, will be produced.

PAUL G. LAUFFER

Cross-references: *Amino Acids, Proteins, Carbohydrates, Adsorption*

COTTRELL, FREDERICK GARDNER (1877-1948)

Frederick Gardner Cottrell was the first to apply the principle of electrical precipitation of suspended dust and droplets from chimney or other gases. The device became the electrical precipitator, which now bears his name.

The simplest construction of a Cottrell precipitator would include a vertical pipe, in the central axis of which hangs an insulated metal wire. The pipe is grounded. A unidirectional high voltage current, varying from 15,000 to 100,000 volts in the different installations, is fed to the wire, so that a powerful electric field is created. Dusty air or fumes travel up the pipe; the electric field ionizes the air or gas; the ions in turn charge the suspended particles by contact. The charged particles travel to the relatively uncharged wall, there depositing the negatively charged particles. Periodically the pipe is rapped so that the deposit drops down into a container box. Suspended droplets are similarly deposited on the pipe wall, where they coalesce and travel downward as a liquid to a suitable outlet. The cleaned air or gas leaves at the top of the pipe.

The unipolar corona discharge is secured by impressing the negative polarity on the wire, which is the discharge electrode. The only exception to this rule are the installations for air-cleaning operations, where the positive polarity is impressed on the wire, because of the lower ozone generation. The Cottrell for full scale smelter or factory installation is more often designed to provide narrow rectangular passages between flat plates, which are then the collecting electrodes, with a series of spaced wires suspended in the center plane of the space. The distance the charged particle travels is a few inches, perhaps 3 or 4, before it strikes the collecting electrode.

Dr. Cottrell began his work on the electrostatic precipitation of dust and droplets in 1910, when he was 33 years old. He was born in Oakland, California, graduated from the University of California, taught high school for a while, then went to Leipzig for graduate studies, coming home in 1902 with the degree of Ph.D. He was instructor and assistant professor at his Alma Mater until 1911. His field of study and research was physical chemistry, and his experimental work in that period were in phase relations, electrochemistry and the liquefaction of gases. From 1911-1921, Dr. Cottrell was successively chief chemist, chief metallurgist and Director of the U. S. Bureau of Mines. From 1922-1927 he was Director of the Fixed Nitrogen Research Laboratory, and after that, he remained as Division chief in the Department of Agriculture.

Tall and thin, always bubbling over with ideas, Dr. Cottrell was a rapid talker, yet at the same time, always modest, unselfish, and little concerned with the acquirement of money or with personal gain. In 1912, he founded the Research Corporation, now of 405 Lexington Avenue, New York 17, to develop electrical precipitation on a large scale for industries, and distribute the profits to researchers for the development of fundamen-

tal research—a lasting and continuing legacy. He advised several other University Foundations on patent administration. In 1948, over \$750,000 were donated to young research workers in the smaller colleges.

Among his other chemical engineering interests were the production of helium from natural gas with a helium content, and the pebble-heat-exchanger as a means of attaining high heat, a project now in process of realization.

E. R. RIEGEL

CRACKING

Cracking is thermal or catalytic decomposition of organic compounds, especially of hydrocarbons and petroleum. Cracking of petroleum products is being used on a large commercial scale for manufacturing gasoline. To a much lesser extent, some petroleum constituents are cracked for making various chemicals, e.g., ethylene is commercially produced by thermal cracking of ethane or propane.

Whereas straight-run gasoline is separated from heavier constituents of petroleum by simple distillation, cracked gasoline is a product of decomposition of heavy fractions, i.e., of gas oil or residues. Heavy hydrocarbons of the latter are cracked or split, forming gaseous and low-boiling liquid hydrocarbons to be used as gasoline. In addition to the decomposition reactions, the cracking process is complicated by condensation reactions involving aromatic and unsaturated hydrocarbons formed on cracking. Thus, high molecular weight hydrocarbons also are formed. The ultimate product of such reactions is the so-called "coke", which actually is a conglomeration of highly condensed polycyclic hydrocarbons. The balance of the decomposition and condensation reactions depends upon the composition of the charging stocks. Those rich in paraffins and naphthenes (cycloalkanes) form less condensation product than those rich in aromatics.

Another factor governing the balance is the extent or depth of cracking. Since the condensation reactions are essentially secondary reactions involving unstable hydrocarbons formed on cracking, they are predominant in the advanced stages of cracking. Hence, in commercial cracking processes the extent of condensation reactions and coke formation, undesirable from the practical standpoint, is controlled by the degree of conversion of charging stocks to cracked products. As a result of controlled conversion, the charging stock is only partially converted into cracked products. A sizable part of the stock remains unconverted or slightly affected by cracking. This is "cycle" or "recycle" stock which can be cracked again after separation, either separately or in combination with fresh charging stock. If the recycle stock is separated and not recycled, the yield of gasoline with reference to the charging stock is specified as the yield per pass. In contrast, the ultimate yield is the yield of cracked gasoline after complete recycling of the recycle stock "to extinc-

tion" and complete conversion of charging stock to cracked products.

The above general conceptions are equally applicable to the thermal and catalytic cracking.

Thermal cracking of petroleum products is carried out at temperatures from 450–550°C for liquid charging stocks (residues and gas oils) to 600–700°C for gaseous hydrocarbons. The rate of cracking follows fairly closely that of first order reactions with the activation energy equal 57,000 Kal. The rate of cracking at temperatures close to 500°C doubles for every 12°C. The pressure is less important, and affects chiefly the secondary reactions. The weak effect of pressure is due to the fact that the cracking reactions at cracking temperatures are irreversible and therefore are not shifted back by high pressures. However, fairly high pressures (from 30 to 50 atm.) are used in commercial cracking mainly due to the favorable effect of high pressures on the heat transfer, elimination of local overheating, compactness of installations, etc. The reaction or cracking time is another critical factor in cracking. The duration of cracking necessary for forming, e.g., 20% (by volume) of gasoline from gas oil are as follows: 4 hours at 400°C, 14 minutes at 450°C and 70 seconds at 500°C.

Catalytic cracking is performed at temperatures from 400 to 525°C. The pressure is atmospheric or slightly higher. The actual reaction time in catalytic cracking, i.e., the actual time of contact of the charge with the catalytic surface is not known. Hence the residence time of the charge in the catalytic reactor is used arbitrarily as an equivalent of the reaction time in thermal cracking. In commercial practice the so-called space velocity (the volume of charge at room temperature passed over the same volume of catalyst per hour) is being used instead of the residence time. The connection between the residence time and the space velocity is obvious: as an example, the space velocity of gas oil equal to 1.0 would correspond approximately to 15 seconds of the residence time at cracking temperatures.

The catalysts used in catalytic cracking are porous heterogeneous compounds of silica and alumina. Silica-magnesia and silica-zirconia catalysts are also active but have a very limited application. Silica-alumina cracking catalysts are either natural clays activated by well known methods or synthetic products obtained by coprecipitation or cogelation of silica and alumina. Since the cracking reactions take place on the surface of catalysts, the surface area of the latter is of primary importance; by this is meant the total surface of micropores of the catalysts, available for adsorption. The surface area of commercial cracking catalysts is very large, of the order of 300–400 m²/gr. For the same catalyst, the activity is proportional to the surface area. (See *Catalysis*).

However, the large surface area per se is not an indication of cracking activity. Pure alumina with large surface area is a very weak cracking catalyst. Likewise, pure silica gel with surface area 500 m²/gr. has no cracking activity at all. The strong catalytic activity of silica-alumina systems is explained by their acidic properties absent in silica

or alumina. The acidic properties of silica-alumina catalysts are responsible for such reactions in the presence of these catalysts under proper temperature conditions, as alkylation, polymerization, isomerization, which are catalyzed by strong acids. The most convincing proof of the acidity of cracking catalysts is the effect of high boiling organic bases, such as quinoline, on their activity. The catalytic activity of cracking catalysts is almost completely suppressed by small amounts of the bases which neutralize the acidic centers and thus suppress the catalytic activity.

The reactions involved in catalytic cracking are much more complicated than those in the thermal process. The primary decomposition and secondary condensation reactions are more or less similar in both processes. However, the condensation reactions on the catalytic surface are more advanced. As a result, no heavy residue is formed; the heavy hydrocarbons are converted to coke. In contrast to thermal cracking, isomerization reactions occur readily in catalytic cracking. Hydrocarbons of thermal gasolines preserve the structure of charging stocks. Hence paraffins and olefins of thermal gasolines have normal structure, if the charging stock is rich in normal paraffins. On the contrary, paraffins and olefins of catalytically cracked gasolines are always branched independently of the original structure of charging stocks. Another reaction specific for catalytic cracking is the hydrogen exchange which takes place, e.g., between naphthenes and olefins, transforming six-membered naphthenes into aromatics and olefins into paraffins. Hence catalytic gasolines are more saturated and more aromatic than thermally cracked gasolines.

Coke formation is an important reaction affecting the activity of the catalyst. The catalyst is extremely active in the first second of the process. Then the activity decreases, at first very rapidly and later gradually, as a result of the deposition of coke covering the active centers of the catalyst. The activity of aged catalysts can be restored by burning out the coke deposited on the catalyst. In commercial practice the catalyst undergoes many thousands of regenerations without losing activity. The mode of catalytic reaction and regeneration are different in three modern catalytic cracking systems.

Fixed-Bed Catalytic Cracking (The Houdry Process) is a system in which cracking and regeneration are carried out alternately in the same reaction chamber filled with catalyst. The charging stock is vaporized and preheated to the cracking temperature in a pipe still and then passed to the reactor. The cracked products are separated in a conventional equipment. The process is periodic and thus requires a very complicated timing equipment controlling alternate reaction and regeneration periods.

Thermofor Catalytic Cracking (TCR) is a process in which the catalyst moves continuously downward in the reactor, usually countercurrently to the vaporized charging stock. The deactivated catalyst passes from the bottom of the reactor to the separate regenerator by means either of a mechanical conveyor or of a gas lift. In the regenerator the catalyst moves countercurrently to

the air, burning the coke deposited on the catalyst. From the bottom of the regenerator the catalyst returns to the reactor by the means mentioned above.

Fluidized Bed Catalytic Cracking is a process in which fine powdered catalyst and vaporized charging stock is mixed with oil vapor in the reactor or with air in the regenerator, forming fluidized bed or suspension of the catalyst in vapor or air. Thus cracking reactions, as well as regeneration, take place in fluidized beds under highly turbulent conditions. Cracked vapors in the reactor, as well as flue gases in the regenerator, are disengaged from powdered catalyst by cyclone separators in the upper part of the reactor or regenerator. The separation of cracked products into gas, gasoline and recycle stock in the Thermofor or Fluidized Bed catalytic units is carried out in conventional distillation and fractionation installations.

The capacity of modern catalytic cracking units varies from 5,000 to 50,000 barrels of charging stock per day.

The yields in catalytic cracking for average gas oils in one-pass operation are as follows: dry gas 7% by weight, gasoline and butanes 47% by volume, recycle stock 45% by volume and coke (on catalyst) 4% by weight. On recycling the ultimate yield of gasoline increases to 60% by volume. As far as the yields of gasoline are concerned, catalytic cracking has no advantage over the thermal process. Its main advantage is due to the high antiknocking properties of catalytically cracked gasoline. While the octane number (Research Method) of an average thermally cracked gasoline is close to 70, that of an average catalytically cracked gasoline is 90.

The total daily capacity of thermal cracking plants in the U. S. A. is 2,355,000 barrels and that of catalytic cracking plants 3,709,000 barrels (January, 1956).

A. N. SACHANEN

Cross-references: *Hydrocarbons, Petroleum, Burton, Catalysis, Antiknock Agents*

CRYOGENICS

Cryogenics, or low-temperature physics, is that branch of science that is concerned with the investigations and the elucidation of natural phenomena that occur at extremely low temperatures. The origin of this phase of science dates back to the time when the so-called "permanent gases", oxygen, nitrogen and hydrogen, were first liquefied. The interest in these gases at the present time has passed largely from physics to industry. In the modern research laboratory they have become essentially 'stock' items.

Today's scientific research at the lowest possible temperatures is dependent mostly on the availability of liquid helium (b.p. -452.0°F or 4.2°K). The liquefaction of helium gas was accomplished for the first time in 1908 by H. Kamerlingh Onnes (1853-1926) at the first organized Low Temperature Laboratory located at the University of Leiden, Holland. By pumping the vapors away from the surface of the liquid helium, thus cooling

the latter by evaporation, Onnes ultimately reached a temperature within 0.7 degree ($^{\circ}\text{K}$) of absolute zero (-459.7°F or 0°K). This still represents the lowest temperature that can be attained without resorting to the newer techniques of adiabatic demagnetization, first suggested independently by W. F. Giaque and Peter J. Debye. By this method temperatures close to 0.001°K have been obtained both at the Clarendon Laboratory, Oxford, England and the Leiden Laboratory, Holland.

In addition to liquefying helium for the first time, Onnes discovered the phenomenon of superconductivity (in mercury) in 1911. This revealed one of the most impressive of all phenomena that occur within a few degrees above absolute zero. Since Onnes' discovery other materials have been known to become superconductors. Certain metals such as tantalum, mercury, lead, tin, aluminum, et al.; certain alloys such as PbTi_2 , Au_2Bi , PbSb , PbAsBi , et al.; and compounds such as VN , CbN , CuS , V_3Si , etc. become superconductors at temperatures close to absolute zero. Below a particular temperature, that is different for each substance, a wire of the material will lose all its measurable resistance to the flow of electric current. A sheet or disc of the same material below this temperature (transition temperature) will become a good screen against magnetism. This observable fact in these various substances is today certainly the most intriguing and the most challenging both from the scientific and practical point of view.

In addition to the existence of the phenomenon of superconductivity, there is one equally fascinating that occurs in liquid helium itself. Below 2.19°K helium enters a new state, which does not resemble a solid, a liquid or a gas. For this reason it has been termed a "fourth state" of matter. The liquid in this "super fluid" condition can creep up the sides of the containing vessel. It has a very high coefficient of thermal conductivity, loss of inertia (quantum fluid), etc.

Some metals, instead of becoming superconductors at these low temperatures, show an increase in resistance with decreasing temperature (resistance minimum). Small amounts of chemical impurities seem to cause this behavior. Resistance minima have been observed in such substances as copper with small amounts of tin as impurity. In still other substances such as copper with small amounts of manganese as impurity, not only is a minimum in resistivity exhibited, but at still lower temperatures a maximum is observed. Specific heats of all materials show a decided decrease when compared to their room temperature values. For common metals this low-temperature value may be less than 1/1000 of that at room temperature. Rapid changes in resistance with temperature, and these extremely small values of specific heats of a particular substance, may be combined in a controlled manner to make the material an extremely sensitive bolometer (i.e., a detector of radiant energy). Magnetic properties of matter are greatly changed at these low temperatures. Insulators like sapphire or diamond become nearly perfect in the liquid helium temperature region. These are but a few of the many

interesting phenomena that occur at extremely low temperatures.

There are a number of ways of attaining them. The most widely used method in the past has been that called the Joule-Thomson regenerative cycle. This technique is simply a sequence of compression, heat exchange and expansion. The gas cooled by this process is used to cool the incoming gas, so that as the process goes along the gas gets colder and colder until it finally liquefies. In case of helium the Joule-Thomson effect becomes operative only after the gas has been cooled to the temperature of liquid hydrogen.

The second method of liquefaction, which has only recently become commercially successful, is to allow the helium gas to drive an engine so that it has a portion of its thermal energy converted to mechanical energy. Helium at room temperature is very much like water when the latter exists far above its boiling point. Such an helium-engine type of apparatus has been developed by S. C. Collins of M.I.T., appropriately called the Collins Helium Cryostat. The availability and wide use of this machine has greatly accelerated low-temperature research activity. In addition to the development of this liquefier, large metal thermos containers or Dewars have recently been designed and constructed and by their use, liquid hydrogen and liquid helium can be stored for several weeks. For maintaining these low temperatures during an experiment, apparatus (or cryostats) have been designed to accommodate standard electrical and mechanical research equipment.

The techniques developed for the measurement of temperature in these low-temperature regions give a precision in measurement still unattainable in research carried out at higher temperatures. Detection of temperature differences of the order of 0.0001°K is quite commonplace. Temperatures can be measured conveniently by the utilization of the electrical resistance-temperature characteristic of fine metallic wires (platinum, gold) or the change in the same characteristic of small commercially available carbon resistors. These types of thermometers are usually referred to as resistance thermometers. They are only useful after their resistance characteristics have been carefully correlated with the absolute scale of temperature. The most convenient thermometer is the thermocouple. However, at extremely low temperatures its sensitivity falls off rather rapidly. Over limited temperature regions the measurement of the vapor pressure of the refrigerant liquid itself serve as a convenient thermometer. For example in the temperature region 0.9 to 4.2°K (-458.1 to -452.0°F) the vapor pressure thermometer appears to be the most satisfactory. The primary thermometer that gives the absolute temperature is the gas thermometer. The pressure variation with temperature of a known amount of gas (e.g., helium) kept at a constant volume is carefully measured. From the equation of state of the gas relating pressure (P) and volume (V), temperature (T) can be evaluated. The gas thermometer, however, represents a rather elaborate piece of apparatus. Only a few laboratories in the world are equipped with such a unit. The apparatus is used

mostly to calibrate secondary thermometers such as the resistance thermometers or thermocouples.

WARREN DE SORBO

Cross references: *Gases*

CRYSTALS AND CRYSTALLOGRAPHY

The term "crystal" (derived from the Greek word meaning ice and originally applied only to crystals of quartz which the ancient philosophers believed to be congealed water) refers to the regular polyhedral form bounded by smooth surfaces which is assumed by a chemical compound (or element) under the action of its interatomic forces, when passing under suitable conditions from the state of a liquid (melt or solution) or gas to that of a solid. Thus a crystal is characterized by its definite external form which is an important manifestation of a definite ordered internal structure—a fact which was proved conclusively in 1912 by von Laue by the diffraction of x-rays from a crystal acting as a three-dimensional grating.

A crystal is the *normal* form of solid chemical elements, compounds and mineral species, but the conditions suitable for the formation of a crystal of ideal perfection in symmetry of form and smoothness of surface are rarely if ever realized. Many solid species may not appear to have geometrical external morphology, even though a definite internal lattice arrangement of atoms or molecules is proved by x-ray diffraction. Such a specimen is said to be *massive*, though crystalline. If this structure, as shown by cleavage, or by optical or x-ray means, is the same in all parallel directions through the mass, then it is a single individual; but if it varies from grain to grain or fiber to fiber, it is a polycrystalline aggregate. If a definite internal repeating plan is lacking, and all directions in the mass are the same, then the solid is *amorphous*, as is true of a glass, which is really a very highly viscous super-cooled liquid. Many substances may be solidified in the glassy state after fusion but will devitrify or crystallize under proper conditions to the more stable state. The common idea that a railroad rail or a bridge may fail because the metal "crystallizes", is erroneous, since the structure is always a crystalline aggregate which may weaken as a result of grain growth and deformation.

The importance of the crystalline state cannot be overestimated. The effort is being made continuously to produce single crystals of increasingly complex materials synthesized in life processes. An outstanding achievement was the crystallization of the tobacco mosaic virus with the retention of infectivity, by Dr. Wendell Stanley, for which he received the Nobel Prize. The x-ray diffraction patterns of single crystals lead not only to the discovery of the regular repeating plan of atomic or molecular building blocks, but also to a revelation of the "motif" or molecular configuration, for example of penicillin, thereby leading to its synthesis in the laboratory.

The science of *Crystallography* includes the description of the observable habit or morphology of crystals in their various forms and of their division into systems and classes; of the methods of

studying crystals, including the determination of the mathematical relations of their faces and the measurement of angles between them; a description of compound or twin crystals, of irregularities and of aggregates; of many physical, optical, electrical and magnetic properties; and as a culminating step the determination and quantitative description of internal atomic structure in terms of electron density distributions in space.

There may be a great diversity of outer form or "habit" of crystals of the same pure element or compound, but the angles of inclination between like faces on the crystals of any species are essentially constant. These angles constitute one of the important distinguishing characteristics of a species. They are measured by an optical instrument called a goniometer, from the angles between reflected beams of light from contiguous faces. The faces are arranged according to laws of symmetry, which permit assignment of crystals into systems and classes. On the basis of optical examination it is a matter of experience that there are 7 arrangements of crystallographic axes, depending upon angles between axes and unit lengths along axes, into triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, rhombohedral and cubic systems. The symmetry operations are mirror planes, rotation axes (1, 2, 3, 4 and 6-fold), and rotation-inversion axes of which the center of symmetry is the most familiar special case. These symmetry elements, singly or in combination around a single point in space, lead to 32 crystal classes or point-groups, divided among the 7 systems. In classical crystallography these classes were given specific names, but they are now generally designated by simple symbols which help to define and describe the much finer classification provided by x-ray diffraction analysis in which outer form is of minor importance.

Optical crystallography goes considerably further than the observation of outer form by means of light. Each class of crystals will have characteristic optical properties revealed by transmitted or reflected light, the observation of which may lead to specific identification of species. First is the index of refraction (see *Refractive Index*) usually measured by means of a refractometer or a microscope. All crystallized substances may be divided into two principal optical classes: isotropic (cubic) in which light has the same velocity independent of the vibrational directions; and anisotropic in which the velocity varies with the direction of vibrations. The latter class is further divided into uniaxial crystals (tetragonal and hexagonal) and biaxial crystals (orthorhombic, monoclinic and triclinic). In anisotropic media a double refraction occurs; this permits plane, circular or elliptical polarization of light by such crystals as tourmaline—the basic principle involved in optical instruments such as the polariscope. Thus, depending on refractive indices, the polarization of light by crystals and the use of polarized light to examine crystals, the production of interference figures, the property of exhibiting different colors in different crystallographic directions by transmitted light (pleochroism), the optical dispersion in certain directions in crystals of white light into its primary colors, and other related observations

with light as a tool including excitation of fluorescence, the science of optical crystallography has developed as a powerful method of identifying and classifying crystals, especially with regard to the 7 systems.

About 60 years ago it became evident that classification of crystals into 32 point groups by optical examination was still too rough to permit an explanation of differences in many properties of crystals belonging to the same point group. Account had to be taken then of internal 3-dimensional structures and symmetries. Thus was introduced the concept of the space lattice, a repeating plan in space, of which there are 14 distributed among the 7 axial systems. When appropriate point groups representing symmetry around a single point are translated to equivalent points of a lattice, additional microsymmetry elements are introduced, namely screw axes and glide planes, revealed only in x-ray patterns but isomorphous with outwardly apparent rotation axes and mirror planes, respectively. The classification of crystals can now be made in 230 space groups, the criteria for which are found only in x-ray diffraction patterns (see *X-Ray Diffraction Analysis*). Thus has arisen with the aid of geometric theory the science of *x-ray crystallography*, which is concerned with the 230 ways in which atoms and molecules can be arranged in regular array in space, and with the final advanced step of determining from intensity data the exact configuration of atoms within molecules which are acting as the "points" in a lattice, from an analysis of electron density distribution within the unit crystal cell. The x-ray crystallographer builds on the information provided by the older classical science of optical crystallography by means of radiation with wave lengths of the order of only one ten-thousandth those of light and therefore capable of revealing the ultimate architectural plan.

Properly included under the subject of Crystallography are also many other techniques which may aid in the description and prediction of behavior of crystals, as follows: (1) *mechanical characteristics*: cohesion, elasticity, cleavage, etch-figures, corrosion forms, fracture, hardness, tensile strength, etc.; (2) *specific gravity*; (3) *heat characteristics*: fusibility, thermal conductivity, expansion coefficients, specific heat; (4) *electrical characteristics*: electrical conductivity and the distinction between conductors, semiconductors and insulators; electrical discharge figures, which may identify the point-group symmetry; frictional electricity; pyroelectricity (the development of electric charges on a crystallized body by heating); piezoelectricity (the development of charges by pressure or tension); thermoelectricity (developed by two unlike solids in contact to constitute a thermocouple); (5) *magnetic characteristics*: magnetic permeability and paramagnetic or diamagnetic susceptibility—a sensitive method of indicating, for example, departures from planar configuration in aromatic compounds, the general shape of a molecule, its approximate position in the crystal framework, bond distribution and effects of substituent groups.

GEORGE L. CLARK

Cross-references: *X-rays, Chemical Microscopy*

CURIE, MARIE SKLODOWSKA (1867–1934)

Marie Sklodowska was born at Warsaw in 1867 and received her early training from her father. In 1891 she went to Paris to study. In Paris she met Pierre Curie in 1894 and they were married the following year. Becquerel's discovery of the radioactive properties of uranium was the starting point for an intensive study by the Curies. In 1898 they announced the isolation of Polonium from the bismuth fraction of pitchblende. They devised an entirely new technique in the search for radioactive materials, based on the idea that radioactivity was an atomic property. Therefore, irrespective of the chemical treatments, the active fraction could be recognized by specific properties, e.g., the ionization of the atmosphere. Using this approach, they succeeded in 1912 in isolating radium as a pure salt. The Nobel prize in physics in 1903 was jointly awarded to Becquerel, Marie and Pierre Curie.

After the death of her husband, Madame Curie accepted his chair at the University. In 1910 she published the classic "*Traité de Radioactivité*". In 1911 she was, once more, awarded the Nobel prize, this time for chemistry, "For her services to the advancement of chemistry, by the discovery of the elements radium and polonium, by the isolation of radium and the study of the nature and compounds of this remarkable element". She also observed the tremendous energy which radium gives off without apparent loss of weight. She was the first to postulate that radioactivity is a fundamental atomic property. Her contributions form the basis of subsequent studies of the chemistry of radioactive compounds.

BERNARD JAFFE

Cross-references: *Radiation, Radium*

CUTTING FLUIDS

A cutting fluid may be any liquid or gas used to cool and lubricate the cutting tool. Its ultimate purpose is to reduce the unit cost of a machining process. In practice, most fluids are oils, water solutions, or oil-in-water emulsions, and their application is largely confined to the machining of metals.

Composition. The oils are usually based on petroleum fractions which, alone, afford minimum cooling, lubrication, and rust protection. Elemental sulfur, fatty acids, fatty oils (lard, tallow, sperm, rapeseed), sulfurized fatty oils, and any of a large number of chemically active sulfurized or sulfochlorinated organic compounds (extreme-pressure agents) may be added in various combinations to control tool pick-up, surface finish, and tool life.

Commercially, oil-base fluids are classified as "inactive" or "active", depending upon their reactivity toward metals. Inactive oils often contain 5 to 25% fatty oil and sometimes about 1% fatty acid. Sulfur may also be added, but only in a relatively unreactive form, such as the reaction product of sulfur and unsaturated fatty oil.

A light-colored active oil may be prepared by dissolving about 1% elemental sulfur in mineral

oil at 180 to 250°F. Black active oils are made by heating 2 to 3% elemental sulfur in mineral oil at 400–500°F, but these usually have a strong odor. A more versatile product, containing 2 to 3% S and about 1% Cl, may be made by reacting sulfur monochloride with mineral oil at 400 to 500°F. Supplementary extreme-pressure agents (e.g., chlorinated paraffin wax, sulfurized terpenes) may be added to these active bases.

"Soluble oils" (i.e., cutting fluids which are designed to form oil-in-water emulsions) are composed of mineral oil, emulsifying agents, and coupling agents. Typical emulsifying agents are sodium petroleum sulfonate and potassium rosin soap, sometimes blended to balance stability and economy. Naphthenic acid soaps, phenates, and synthetic emulsifiers may also be used. Coupling agents, e.g., glycols or alcohols of 100 to 200 molecular weight, prevent gelling of the concentrate and stabilize the final emulsion. Germicides, wetting agents, and water softeners may be present as well.

Cutting fluids sold as heavy-duty soluble oils generally contain a fatty oil or an oil-soluble extreme-pressure agent or both, which enhance the load-carrying properties if the water/soluble oil ratio is not larger than about 10/1 in the final emulsion.

Water-solution cutting fluids, also known as chemical-type fluids, contain little or no mineral oil and are primarily concentrates in water of ar rust agents, such as sodium nitrite and triethanolamine. The better fluids also contain wetting and load-carrying agents, which greatly augment their performance. Germicides, buffers, and solubilizing agents may be included.

Function. A cutting fluid improves the efficiency of production through mechanisms which depend upon its composition and the requirements of the application. Classically, the mechanisms are listed as cooling, lubricating, and prevention of welding. The properly selected cutting fluid balances these functions, thus providing optimum tool life to yield a maximum production rate for a specified surface finish.

Cooling is important because cutting tools lose their hardness rapidly above 800 to 1000°F, with consequent accelerated wear and mechanical failure of the tool point. Such temperatures may easily be reached when alloy steels are cut at moderate to high speeds, and water-base fluids must then be used for adequate cooling. Oil-base fluids reduce friction, but this effect does not compensate for the superior heat transfer obtained with water-base fluids in high-speed cutting.

Oil-base fluids are advantageous where surface roughness or tool forces must be kept to a minimum, or where seizure must be prevented. Good finish may be obtained with almost any fluid by taking very fine cuts at high speed. However, with chip dimensions that give economical rates of metal removal, surface roughness is determined mainly by the "built-up-edge" (particles of the workpiece welded to the tool point during the cutting operation). Boundary-lubrication agents (fats and fatty acids) and extreme-pressure agents are blended with mineral oil to provide the desired

degree of antiwelding action without significant sacrifice of tool life from excessive chemical corrosion. The optimum balance of these agents will vary with the nature of the metal-cutting process and the operating conditions.

Tool forces are important when working with tools of marginal strength (small taps and drills), marginally powered tools, or easily deflected workpieces. By virtue of their lubricating properties, oil-base fluids containing extreme-pressure agents are most effective in reducing tool loads. Moreover, they also alter the direction of the resultant force on the tool. The latter effect can sometimes be adjusted to alleviate tool vibration (chatter).

In addition to its primary metal-cutting functions, a marketable product must provide secondary service benefits and should entail only a minimum of inconvenience. Thus, cutting fluids must protect both machine and workpiece from rust, remove chips from the cutting zone, and in many cases they are also expected to lubricate the exposed mechanisms of the machine. Only a minimum of smoke, fog, odor, stain, or instability may be tolerated. Moreover, considerations of toxicity exclude many materials. These secondary properties are often taken as the principal criteria for cutting-fluid selection because of their psychological importance and the relative ease with which they are evaluated.

Application. Each machining process (broaching, drilling, sawing, etc.) may require a different combination of cutting-fluid properties for best performance. Moreover, each process may be carried out in various machines of different power and speed capacities, which therefore require slightly different cutting-fluid properties. Furthermore, each metal brings special problems to the field. Thus, steels vary widely in machinability; copper alloys stain when in contact with active sulfur; magnesium involves fire and electrolytic-corrosion hazards with water-base fluids; and the special problems for titanium are still being evaluated. While there are no universal cutting fluids, some are less sensitive to operating variables than others. Hence, although they do not provide maximum performance, they are likely to be more trouble-free over a wide range of applications.

Economics. Various estimates from current surveys indicate an annual United States cutting-fluid sales volume of 60 to 80 million gallons, with double this rate during wartime. From 25 to 35% of the fluids used are water-base, and about one-fourth of this is the solution or chemical type. Of the larger fraction (viz., oil-base fluids) about two-thirds are premium-quality heavy-duty compounded oils and one-third are economy-grade oils. It may be expected that, with increasing use of carbide tools which permit high cutting speeds, the water-base/oil-base ratio will gradually increase.

If it is assumed that cutting-fluid sales parallel the distribution of metal-working plants, about one-third of the market is concentrated in Ohio, New York, and Illinois, with California, Pennsylvania, and Michigan each accounting for 6 to 10%.

Oil-base fluids sell for 30 to 70 cents per gallon,

depending on the additive content, and water-base fluids sell for 40 cents to several dollars per gallon of concentrate before dilution. The total value of these products was about \$30 million in 1955.

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Cross-references: *Lubrication, Lubricating Oils, Emulsions*

CYCLIC COMPOUNDS, see ALICYCLIC COMPOUNDS, HETEROCYCLIC COMPOUNDS

CYTOCHEMISTRY

The microscopic cells of which all plants and animals are composed are essentially similar in that they consist of living protoplasm and, in most instances, a limiting membrane. The study of the variations in form, function and life-histories of many different types of cells has developed into the important branch of biological science known as *cytology*, which deals with individual cells and their intrinsic characteristics. The chemical identifications of the materials which make up the cells constitute that branch of cytological investigation known as *cytochemistry*. In its broadest sense cytochemistry includes the determination of the chemical constitution of all protoplasmic and cell membrane constituents at all stages of development of the cell. These determinations are carried out at suitable magnifications, with the least possible damage to the structural organization of the cell.

The substances identified by the earlier workers in the field of cytochemistry were often those which were either most conspicuous or most abundant. The carbohydrate *starch* was observed to exist in the form of comparatively large grains and to be located in special plant cell organs named *chloroplasts* and *leucoplasts*; found to be a temporary storage product produced from *sugar*; and later reconverted to sugar and translocated, from the cell in which it was formed, either to growing regions of the plant or to organs, such as tubers, where it was again converted to starch for permanent storage. *Proteins*, important constituents of all protoplasm, were found to be of many types and to occur in varying concentrations in the nucleus and other cell organs as well as in different regions of the cytoplasm. Such phenomena involve chemical processes which are not fully understood even today. This pioneer work, in its most elementary form, required a background of training in biology, physics and chemistry upon the part of the investigators. The information which they accumulated constitutes the framework within which much of the current cytochemical research is carried out.

More recently starch grains have been found to contain only 80 to 85% "starch substance"; the additional components consist of such materials as fats, tannin, phosphates, water and even hemicellulose. The main component has been further subdivided into mucilaginous *amylopectin* and *amylose*, a denser, less reactive material. The chemical constituents and physical components of

the starch grain lend themselves to cytochemical investigation and starches of many types are being studied intensively. Proteins have been shown to be formed by the union of *amino acids* such as *tyrosine*, *tryptophan* and *phenylalanine*. Numerous qualitative cytochemical methods for the identification of specific amino acids or amino acid groupings have been developed, some of the more common of which are the Glycolic Reaction, Voisin's Reaction, Xanthoproteic Reaction and Biuret Reaction.

The requirements of modern cytochemical research are rigorous. Standards of precision are far beyond those required in earlier cytochemical investigations. Optical principles involved in the formation of images in the microscope must be recognized in greater detail than was required for the microscopical examination of fixed and stained materials; artifacts must be avoided; diffusion of the substance under investigation from its normal location in the living cell must be detected and, if possible, prevented. Freeze-drying and special methods of fixation have contributed to a more normal condition of the cellular materials to be studied. The polarizing microscope, the ultraviolet microscope, the fluorescence microscope, the infrared microscope, the electron microscope and the microspectroscope now supplement the ordinary light microscope in obtaining cytochemical data. Such accessory techniques as microincineration, electrophoresis, chromatography, x-ray diffraction, electron diffraction and tracer methods provide background information which contributes to the accuracy of cytochemical interpretations.

In view of the highly specialized nature of many of these methods of analysis, a cytochemical study is now frequently conducted by a group of highly trained specialists rather than by a single individual. Within the last two decades, important advances have been made in cellular chemistry by investigators such as Caspersen, Linderström-Lang, Lison, Feulgen, Commoner and their associates. Improved methods are now available for the cytochemical determinations of such a wide variety of substances as nucleic acids, pigments, aldehydes, enzymes and bacteriophages. New information furnishes a sound basis for more critical examination of past theoretical conceptions of such fundamental cellular processes as protein and carbohydrate syntheses. New cytochemical approaches are being developed in the fields of plant and animal nutrition, in the kinetics of reproduction and in the pathogenesis of viral and bacterial infections and sarcomas. Many of these methods fail to meet the highest standards of significant cytochemical identifications and efforts to replace and improve them are constantly in progress. Cytochemistry is now established, however, as an important branch of cytology. Its fulfillment in terms of one of the most dynamic methods of investigation in the field of biological sciences lies in the future.

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Cross-references: *Carbohydrates, Chemical Microscopy, Proteins, Amino Acids, Protoplasm*